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FULL-SCALE DESULFURIZATION OF STACK GAS BY DRY LIMESTONE INJECTION. VOLUME I

F. E. Gartrell

Tennessee Valley Authority
Chattanooga, Tennessee

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The report gives results of a test program of dry limestone injection, demonstrated on a 150-Mw pulverized-coal-fired boiler at TVA's Shawnee Plant. The program included: equipment shakedown, dust distribution studies, process optimization, and long-term injection trials. It identified major process variables; evaluated distribution of lime dust in the boiler, effect of operating variables on distribution, and resulting effects on SO2 removal; evaluated the sensitivity of SO2 removal to key operating and process variables; evaluated conditions for optimum SO2 removal; studied process effects on boiler operation and maintenance, on solids collection equipment, and on water quality; and completed a process economics study. The program is discussed in context with previous investigations and EPA-sponsored support activities. Appendices contain test program detail results and results of EPA support projects. Because of low SO2 removal efficiencies and the potential for major reliability problems, it does not appear that dry limestone injection will play an important role in controlling SO2 emissions from power plants.

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VOLUME I

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Chattanooga, Tennessee

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ABSTRACT

Dry Limestone Injection was demonstrated on a 150-MW pulverized coal-fired boiler at TVA's Shawnee Steam Plant. The test program consisted of: (1) equipment shakedown, (2) dust distribution studies, (3) process optimization, and (4) long-term injection trials.

The test program: (1) identified major process variables; (2) evaluated distribution of lime dust in the boiler, effect of operating variables on distribution and resulting effects on SO_2 removal; (3) evaluated the sensitivity of SO_2 removal to key operating and process variables such as SO_2 concentration, excess air, reaction zone residence time, temperature of injected limestone, stoichiometry, limestone type, particle size, and unit load; (4) evaluated conditions for optimum SO_2 removal; (5) studied process effects on boiler operation and maintenance, on solids collection equipment and on water quality; and (6) completed a process economics study.

The program is discussed in context with previous investigations and EPA sponsored support activites. Appendices contain test program detail results plus results of EPA support projects. A summary of results and conclusions is presented as a complete evaluation of the capability and potential application of the process.

In light of the inherently low SO_2 removal efficiencies and the potential for major reliability problems, it does not appear that the dry limestone injection process will play an important role in controlling SO_2 emissions from power plants.

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CONVERSION TABLE

EPA policy is to express all measurements in Agency documents in metric units. When implementing this policy results in undue cost or difficulty in clarity, the National Environmental Research Center-Research Triangle Park (NERC-RTP) provides conversion factors for the particular nonmetric units used in the document. For this report these factors are:

British		Metric
Multiply	By	To Obtain
feet	3.0480×10^{-1}	meters
feet^2	9.29×10^{-2}	meters^2
feet/sec.	3.0480×10^{-1}	feet/sec.
feet^3 /min.	4.720×10^{-1}	liters/sec.
grains (troy)	6.48×10^{-2}	grams
grains/dry s.c.f. @ 70° F	2.464	grams/meter^3 @ 0° C
gallon	3.785	liters
inch	2.5400×10^{-2}	meters
micron	1.0×10^{-6}	meters
ounce (troy)	3.1103×10^{1}	grams
pound	4.536×10^{-1}	kilograms
pound/in.^{2}	7.03×10^{-2}	kg/cm^2
quart	9.463×10^{-1}	liters
tons/hr.	2.520×10^{-1}	kg/sec.

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SUMMARY AND CONCLUSIONS

TVA Test Program

Report Scope

Volume 1 of this 3-volume report covers the main text of the test program that was conducted by TVA at the Shawnee Steam Plant. It covers the equipment used, the tests carried out, and the results obtained. Conclusions are given for the results that were obtained in the tests to remove sulfur dioxide from stack gas.

Volumes 2 and 3 are both appendices to Volume 1 but contain, in addition, the results of support projects which were separately funded by the Environmental Protection Agency. Some appendices contain references in addition to those given in Volume 1 which also has both general references and a bibliography.

Utilities are primarily interested in knowing how effective is dry limestone injection for SO_2 removal and what effects the process has on the boiler, on its solids collection system, and on the disposal water quality. Capital and operating costs being projected for the process are shown in a 52-case parametric study. Included is an EPA review of important limestone factors and how they influence SO_2 removal; where sources of limestone exist and its general availability. The important aspects of utilization of large tonnages of limestone modified fly ash resulting from the process are thoroughly reviewed.

General Assessment of the Dry Limestone Injection Process

The apparent simplicity of injecting dry, pulverized limestone into a boiler to achieve sulfur dioxide removal and the need to confirm or improve on the results already achieved by other researchers were major factors in selection of the process for full-scale study. Other factors such as use of a widely available reactant, limestone, prepared in conventional equipment and applicable in a retro-fit way to existing boilers were also assets.

The process suffered from the low SO_2 removal rates achieved during intensive testing in which limestone feed rates at and beyond practicable values were employed. At 2X stoichiometric, the Fredonia limestone achieved only 18% SO_2 removal under full load boiler conditions. Two other limestones thought to be capable of good removal gave similar results: marl with 20% and aragonite with 17%, under the above injection conditions. Higher injection rates gave improved removals of SO_2 but these injection rates were impractical. The two most influencial factors on removal were found to be the rate of limestone injection and the residence time of the particle in the optimum temperature range for the reaction. This temperature range is from 1700 F to 2200 F. At Shawnee this range exists at full load from the arch up into the secondary superheater. The longer particle residence time was achieved with half load on the boiler which increased SO_2 removal to an absolute of 26% with Fredonia limestone at 2X stoichiometric. The turbulence of furnace gas greatly influences and perhaps overrides the effects of other imposed variables such as the angle of injection, velocity of injection, limestone particle size, among others. Load reduction results in better SO_2 removal rates and lower total emission but also reduces stack exit velocity. Thus, a more efficient SO_2 removal is obtained at the expense of lower electrical output.

The second major drawback of the process experienced at Shawnee was plugging of the boiler reheater and the hydroveyors used to sluice fly ash. Even 1X stoichiometric feed rate as used in the second attempt at long term injection would ultimately have resulted in intolerable pressure drop across the reheater. The reheater became plugged and caused the unit to be removed for cleaning during the Trial 1 of long term injection. The loss of generation and cost associated with this kind of cleanup are serious process deficiencies. Increased erosion of heat transfer surfaces and ash handling equipment must be taken into account.

Extensive testing showed that precipitator performance was poorer with limestone injection because maximum corona input power density attainable was lower. Although the mechanical collector was relatively insensitive to the process, the overall efficiency of the dust collection system varied broadly between 72% and 99% depending significantly on precipitator performance. With limestone injection the effect of sulfur on the precipitator appeared to be random but moisture conditioning at lower temperature was evident. To maintain precipitator efficiency at pre-limestone injection level, its size would have to be increased by a factor of 3.25 if fine size limestone were used and outlet gas temperature was held at 309 F, for instance. An added cost of $7.20/kW would be required to build precipitator capability to meet pre-injection gas conditions. Plants like Shawnee which recently were outfitted with precipitators would require new and expensive programs to maintain dust emissions at pre-limestone injection levels.

The waste disposal system is affected in three ways by the process. The quantity of liquid effluent increases, the quality of disposal pond water is altered, and more suspended solid waste which alters settling characteristics is incurred. These effects may combine to create a disposal pond effluent that exceeds effluent standards and degrade the quality of receiving streams. Shawnee test results showed that limestone injection affected sluice water by changes in pH, dissolved solids concentration and hardness. Large steam plants on small streams, under stringent effluent limits of some parameters, would probably require closed-loop operation or treatment. Such treatment for the 10-unit Shawnee plant is estimated to cost $4 to $6 million annually for capital and operating costs under injection conditions. The presence of some heavy metals dissolved in the effluent could adversely affect costs by limiting limestone selection to those with low levels of such metals. The process thus imposes new problems for waste water quality not encountered without injection.

Process costs consist of expenditures for capital investment, operation and maintenance. Unit investment was shown to range from $5.8 to $36.8 per kW depending on unit size, sulfur in coal and injection stoichiometry. An economic analysis for plants having 15 years or less of operating life showed that low sulfur coal installations would have lower total operating cost but that operating cost per ton of sulfur removed is notably higher for such installations.

In light of the inherently low SO_2 removal efficiencies and the potential for major reliability problems, it does not appear that the dry limestone injection process will play an important role in controlling SO_2 emissions from power plants.

Specific Results of the Shawnee Test Program

A four-phase program consisted of: (1) shakedown and preliminary operation of all equipment, (2) a dust distribution study to assess how well injected limestone was mixed with furnace gas, (3) an optimization phase to learn which variables produced the most significant effects, and (4) trials to inject limestone under optimized conditions for study of long-term effects. Operation of a nominal 20 ton per hour limestone preparation and injection system with ability to inject at three (later four) different boiler elevations provided the necessary capability for this test program.

Sufficient on-site laboratory equipment provided for rapid analyses of coal sulfur content and limestone fly ash dust samples. Continous SO_2 monitoring was done by ultra violet analyzers on flue gas sampled at the boiler outlet. These analyzers were the principal instrument for SO_2 removal determinations. The many variables and the thousands of analyses induced the statistical approach to test design and evaluation of results. Off-site, concurrent studies using some inputs from Shawnee searched for mathematical models to describe the physico-chemical process that must accomplish SO_2 removal in a second or less in the boiler. The very important effects the process had on precipitators and on disposal water quality are discussed in this Summary and Conclusions section and are fully evaluated in the appendices of this report. Attempts during the dust distribution phase to "see" the dust in the furnace gas led to the interesting use of laser holography—a first in such application. The end of on-site testing came after the second of two brief continuous injection periods that proved the Shawnee reheaters capable of being plugged by limestone induced deposits.

Phase I

Statistical analysis applied to all Phase I (equipment shakedown and preliminary tests) test data failed to identify any statistically significant relationship between test variables and limestone distribution and sulfur dioxide removal. No variable was significant for any of these tests. The most significant information derived from Phase I was recognition of an uncontrolled and previously unidentified variable—gas turbulence pattern.

SO_2 removal increased by 8% (absolute) per unit stoichiometry as the injection elevation was moved from the furnace lower rear to upper rear.

Other conclusions were: that coal sulfur variations would make shorter test periods advisable; that lower rear injection (longer time at higher temperature) rendered limestone more unreactive so injection should be moved higher in the furnace for lower temperature and shorter residence time; that water-cooled probes were adequate but other techniques were needed for instantaneous dust distribution measurement; that effects on heat transfer surfaces require more attention to sootblowing and ash sluicing.

Phase II

Furnace gas turbulence is the major variable which has the greatest effect on dust distribution, therefore, attempting to impose outside control over dust distribution yields little effect. Perhaps modification of existing dust distribution patterns is undesirable. Gas turbulence rather than injection elevation controls dust distribution.

Process sensitivity to input variables, controlled and uncontrolled, showed that:

a. Large changes in furnace excess air had little effect on dust distribution.
b. Slagging variations were recognized as possibly contributing to unexplained fluctuations in SO_2 removal in Phase I.
c. Variations in secondary air damper settings definitely influence turbulence patterns as shown by identifiable changes in dust profiles.
d. Holding load, coal and burner settings constant will result in relatively constant CaO concentration profiles.
e. Limestone injection velocity, per se, did not significantly affect dust distribution over the range tested.
f. Limestone injection conditions, such as angle and velocity, were overshadowed by furnace turbulence. Practical installations require a reasonable number of nozzles and mean velocities above 75 feet per second.*
g. Nozzle angle variation did not influence SO_2 removal by detectable amounts.
h. Significant increase in SO_2 removal was obtained by injection at higher furnace elevation where lower gas temperature exists.

Phase III

During optimization testing it was found that SO_2 removal depended mostly on limestone feed rate (stoichiometry) and residence time. Higher stoichiometries and smaller particle size improved absolute SO_2 removal. However, higher feed rates showed decreasing SO_2 removal efficiency or SO_2 removal percent per unit stoichiometry (diminishing returns). Limestone grinding costs and destruction of pore volume (surface area) if ground too fine dictate the minimum mean particle diameter to approximate five microns.

SO_2 removal efficiency improved for each of three limestones tested (marl, Fredonia and aragonite) as particle residence time was increased in the optimum reaction zone temperature range (2200°-1700° F). Marl was most sensitive and aragonite the least to increased residence time.

SO_2 removal is sensitive to limestone type. At 2X stoichiometry, the average removal rates for each type were:

Limestone	Full Load	Half Load
Marl	20%	36%
Fredonia	18%	26%
Aragonite	17%	21%

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*Factors for converting these and other English units to their metric equivalents may be found on page xxiii.

SO_2 concentration influences removal rates. Low initial concentrations yielded lower SO_2 removal efficiencies than when high sulfur coal was burned. Low sulfur coals would not benefit boilers employing dry limestone injection for continuous or episode SO_2 control.

Phase IV

Reheater plugging resulting from only 1X to 2X stoichiometric limestone feed rates that caused excessive pressure drop in the reheater are attributed to a combination of factors whose relative importance could not be clearly identified. Limestone fly ash deposits on the reheater grew rapidly and were of composition that defied removal. Increased sootblowing frequency could not have prevented plugging nor would additional sootblowers have solved this serious problem. Use of a single source coal to minimize ash property variations did not retard or prevent deposits. Altered ash properties and higher solids throughput, combined with close (1") tube spacing, cause plugging. Existing boilers offer little chance of major revision to reheaters (or wherever else plugging develops on heat transfer surfaces) in order to eliminate this problem.

Hydroveyors in sluice lines plugged because the limestone fly ash mixture is more cementitious than fly ash alone. Modifications to this device would be necessary to maintain its usefulness with limestone injection.

Boiler operation or thermal efficiency is reduced to the extent that increased deposits hinder heat transfer, that higher dust burden may increase erosion, and there is a small heat burden of the chemical reaction. Equipment operation for limestone preparation and injection presented a few minor problems but, in general, proved adequate for accomplishing dry limestone injection on a full-size boiler.

Proof of long-term SO_2 removal capability could not be carried out because of plugging mentioned above. It is reasonable to expect removal rates achieved in these two long-term trials could be sustained.

Application of dry injection on other types of boilers, if carried out under similar inputs as Shawnee, would probably yield similar SO_2 removals but ash burdens in slag-tap furnaces might require special study.

In addition to adverse effects on the boiler are the effects on precipitators and on the disposal water quality. The next sections contain conclusion on both of these effects and the process economics.

Limestone Injection Effects on Solids Collection System

This report presents the results obtained from 37 test runs on a full-scale plant firing pulverized coal and having a dry additive injection system. The major variables studied include flue gas temperature into the dust collecting equipment, coal sulfur, and additive stoichiometry and particle size. Two levels of each variable were investigated. These tests and data from other pertinent sources have been analyzed and correlated The results are summarized as follows:

1. The performance of the mechanical collector was relatively insensitive to all test conditions of injection or noninjection ranging between 50 and 60% efficiency. On the other hand, the overall efficiency of the dust collection system varied broadly between 72 and 99% depending significantly on the electrostatic precipitator performance. Without limestone injection, flue gas temperature and volume, and coal sulfur were the critical variables while with injection, the particle size of the additive was another important parameter.
2. The precipitation rate parameter was a significant semi-logarithmic function of the corona power input density.

   $W = 0.47 + 0.16 \ln P_A$ (No Injection)

   $W = 0.52 + 0.12 \ln P_A$ (Coarse Additive Injection)

   $W = 0.46 + 0.14 \ln P_A$ (Fine Additive Injection)

   where,

   W = precipitation rate parameter (FPS)

   P_A = corona power input density (kilowatts/1000 ft^2 of collecting surface)

   In general, the precipitator performance was poorer with limestone injection because the maximum corona input power density attainable was lower, particularly when fine limestone was injected.
3. A correlation of use in sizing electrostatic precipitators was found by examining the effects of the parameters of limestone particle size, flue gas temperature, coal sulfur and limestone injection rate on corona power input density. The correlation resulted in the following equations:

   (coarse)

   $$P_A = -1.435 - 0.336S + \frac{10.0}{L} + \frac{3.87}{T}$$

   (fine)

   $$P_A = -0.990 + 0.199S - \frac{0.694}{L} + \frac{2.74}{T}$$

   where,

   S = coal sulfur fired (tons/hr)

   L = limestone injected (tons/hr)

   T = flue gas temperature ($^\circ F \times 10^{-2}$)

By use of these equations and the correlation between precipitation rate parameter and power density shown above, it is possible to size a precipitator for the following limiting conditions:

Coal Sulfur Fired (S)
1.0 to 3.2 tons/hr
Limestone Feedrate (L)
5.3 to 16.8 tons/hr
Flue Gas Temperature (T)
$(240 \text{ to } 315)(10^{-2})\,^{\circ}\text{F}$.
Stoichiometry 0.28 (L/S) = 1.0 to 4.0

4. Mechanical collector fractional efficiency curves for fly ash alone and fly ash plus additive reaction products were essentially the same ranging from 25% on the 5 micron size to 90 to 95% on the greater than 25 micron size. However, the electrostatic precipitator fractional efficiency curve on fly ash alone was nearly constant over the entire particle size range, i.e., 80 to 90%. With limestone injection, the electrostatic precipitator showed decreasing collection efficiency as particle size increased. The fly ash alone had an average mean size by weight of 19 microns at the mechanical collector inlet while with both coarse and fine limestone injection, the mean size was about 9 microns.

   The average particulate loading at the mechanical outlet-precipitator inlet varied linearly with limestone injection rate ranging from 1.5 grains per scf at 0 feedrate to about 4.0 grains at 16 tons/hr.

5. Laboratory particle resistivity measurements, in general, were higher than in-situ resistivities on samples from the same test both with and without limestone injection.

   The criticality of coal sulfur and moisture on particle resistivity was verified by in-situ measurements without limestone injection, particularly at the lower gas temperatures.

   With limestone injection, the effect of sulfur appeared to be random, but moisture conditioning at lower temperatures was still evident.

6. The precipitation rate parameter degradation as a function of particle resistivity was demonstrated. However, the critical range of resistivity seemed to be occurring in the 10^{11} to 10^{13} ohm-cm range which is somewhat higher than normal.
7. There was no obvious correlation between the chemical composition of the particulate and the performance of the precipitator.
8. An optical sensor installed on the precipitator outlet duct provided a good qualitative indication of boiler and dust collecting equipment operation. There appeared to be a linear relationship between outlet particulate loading and sensor output voltage. However, the necessity for maintaining clean lenses was evident.

9. Using a baseline of 415 pounds emitted/hr and 570,000 cfm of flue gas at 309F, estimated costs of the fly ash only electrostatic precipitator (installed) at 309F was compared with one at 600F. In addition, size modifications and costs for electrostatic precipitators with coarse and fine limestone injection (2 x stoichiometry) were compared at 250, 309, and 600 F.

   The following summarizes the results:

Electrostatic Precipitator Cost and Size Factors		250F	309F	600F
Cost Installed	($/Kilowatt)			
	No Injection	-	2.21	5.85
	Coarse Injection	2.58	3.21	7.10
	Fine Injection	3.44	7.20	7.10
Size Factor	(x no injection at 309F = 1.0)			
	No Injection	-	1.0	2.44
	Coarse Injection	1.17	1.45	2.96
	Fine Injection	1.56	3.25	2.96

Coarse limestone at a flue gas temperature around 250F emerged as the best alternative for the limestone injection cases when only considering precipitator size modificaton.

However, the present Shawnee boiler flue gas is about 300F and would require cooling in order to take advantage of the 250F result. This added cost could offset the difference between coarse limestone at 309F at $3.21/kW and $2.59/kW at 250F. With fine limestone injection, the precipitator size requirements at 250F are still at a minimum but as above, extra cost for gas cooling would be required. The requirements at 309F and 600F are for all practical purposes equivalent.

For coarse limestone injection, the present precipitator on Unit 10 at 309F would have to be increased in size about 45% in order to maintain the desired emission level stipulated above. If it is feasible to reduce the gas temperature to about 250F, the size increase required would only be 17%. On the other hand with fine limestone injection, the size increases at 309 and 250F would be 225 and 56% respectively.

For the grassroots plant, the evaluation shows a cold precipitator (250F) as the best option on a cost basis.

(See appendix F for full report.)

Limestone Injection Effects on Disposal Water Quality

The system for collecting and disposing of ash at Shawnee Steam Plant is typical of many coal-fired electric power plants. The gas stream is routed first through mechanical collectors and then through electrostatic precipitators to remove ash. At Shawnee the solid reaction products and unreacted lime that result from operation of the experimental limestone injection system were removed from the gas stream along with this ash. The ash from hoppers was removed by a water jet-induced vacuum and then pumped to the ash disposal area. After suspended solids have settled, the water used to sluice the ash to the disposal area was discharged to a receiving stream, in this case the Ohio River.

Waste products from the limestone injection system affect the waste disposal system in three ways: (1) they increase the quantity of liquid effluent because additional flow is required to sluice the added volume of waste products; (2) they alter the quality of the disposal pond water; and (3) they increase the amount of suspended solid waste and alter its settling characteristics.

The increased volume and altered characteristics of the sluice water combine to create a significant potential for the effluent from the disposal pond to exceed effluent standards and to degrade the quality of water in the receiving stream.

Comparison of the results of extensive tests of sluice water during limestone injection and during normal operations at Shawnee indicates that the most significant water quality parameters affected were pH, dissolved solids concentration and hardness. Water used to sluice only ash during normal operations at Shawnee is quite alkaline; the addition of unreacted calcium and reaction products during limestone injection not only raised the pH but also highly buffered the effluent so that either treatment or additional stream dilution would be required to neutralize the discharge. Even if the pH of sluice water from normal operations were near 7, the alkalinity added by wastes from the limestone injection process would still be likely to raise the pH above the usually recommended effluent limits of 8.5 or 9.0. Although most regulatory agencies have not adopted effluent standards for total dissolved solids content or hardness, the data from Shawnee Steam Plant indicate that when large plants are located along relatively small streams the usual stream standards may be exceeded. The establishment of stringent effluent limits for these parameters would necessitate either closed-loop operation or treatment.

The increase in sulfate (SO_4) concentrations during the period of limestone injection tests was not great enough to degrade water quality significantly; however, as noted in the test results, the SO_2 removal efficiencies of the limestone injection process were quite low. Higher efficiencies would be expected to result in higher SO_4 concentrations. Other water quality parameters are not as sensitive to SO_2 removal efficiencies as is the SO_4 concentration because other significant dissolved waste results from injection material and are available for dissolution whether the reaction occurs or not.

In addition to their principal constitutents, all limestones contain some heavy metals and other trace elements that are significant because of their detrimental effects at low threshold concentrations. Regulatory agencies are proposing extremely stringent effluent limits for many of these metals and trace elements. Although curtailment of the long-term test phase prevented the collection of sufficient data for an accurate, quantitative assessment of trace elements, sufficient data were collected to indicate the presence of several heavy metals dissolved in the effluent and to indicate their potential for degrading water quality. These indications suggest that before any limestone is selected for use in the injection process, it should be analyzed to determine its soluble metals content. By limiting the choices of limestones that could be used, unacceptably high levels of heavy metals or other trace elements could severely affect the economic feasibility of the dry limestone injection process at some locations.

Projections of data obtained when wastes from the dry limestone injection process were added to the ash sluice water at Shawnee Steam Plant indicate that the pH of effluent from the waste disposal pond would exceed the upper limit for pH in industrial discharges into the Ohio River, the hardness and dissolved solids content would approach levels that are undesirable, and trace metals content would be high enough so that it may exceed future standards. Therefore, treatment of the effluent or closed-loop operation must be considered when evaluating a prototype installation, either of which would increase the cost of this SO_2 control system.

No economically feasible method is known for treating such a large flow to reduce the dissolved solids concentration and hardness. Treatment of the highly buffered pH is also considered impractical. Distillation is, for example, one method considered technically feasible for treatment of the dissolved solids. Treatment by this method would cost $4 to $6 million annually in capital and operating costs for a limestone injection system for the ten units at Shawnee. Reusing sluice water in a closed cycle operation is feasible but it would increase costs because of the needs for additional and larger pumps, larger and longer pipelines, and their more frequent replacement. Very likely the recycle of such high concentrations of dissolved solids would greatly increase maintenance problems.

A detailed discussion of the effects on water quality from operation of the dry limestone injection installation and a tabulation of the data obtained are presented in appendix G. However, certain precautions must be taken in projecting these data. Utilization of other limestones in different modes of operation may create greater or lesser problems. Quality of the waste and its potential for degrading water quality depend on the type of coal, limestone feed rate or stoichiometry, type of boiler, and type of ash collection system. Data obtained during the test phases fluctuated widely, partially because of the complex chemical nature of the sluice water but apparently, and more significantly, because of the variation in input parameters that occurred even during controlled test conditions.

Although the potential for degradation of water quality is evident, the magnitude of the problem cannot be defined accurately for all potential users of the dry limestone injection system. A potential user must try to:

1. Quantify the principal and trace soluble constituents of the system he proposes to use,
2. Determine the acceptability of discharge of this waste in regard to existing and proposed standards and possible damage to the environment, and
3. Evaluate the costs of corrective measures.

The acceptability of such discharges generally has been based on stream standards that allow utilization of residual capacity for dilution in receiving streams. It seems quite apparent, however, that effluent standards will soon be widely implemented and that elimination of all discharges, where feasible is the ultimate goal. These circumstances would seem to require an evaluation of closed-cycle operation for any proposed dry limestone injection system. (See appendix G for full report.)

Limestone Injection Effects on Boiler and Power Plant

At Shawnee the two major operating problems encountered were rapid plugging of the reheater and the hydroveyors. This occurred during Phase IV trials at long term injection. Solids deposition on the reheater could not be handled by existing sootblowers and it is doubtful if additional blowers would have helped. Providing more space between reheater pendants by removing alternate rows might have helped but such an approach is impractical because (1) the deposits might form further downstream and (2) a given boiler requires heat transfer surface where it is presently installed. Major revisions to old boilers other than to install injection nozzles or sootblowers (in cases where added blowers might help) would be very expensive. Even if limestone injection was much more efficient in removing SO_2 yet caused uncontrolled plugging of major components, it could not be used. The hydroveyor plugging required considerable operator attention and lengthened sluicing periods.

Long term injection trials at Shawnee were too short to allow factual assessment of component erosion by injected limestone, either on the boiler or on mechanical collectors. However, there is reason to believe that continuous injection would result in greater erosion in the same areas presently receiving high erosion from fly ash.

Higher ash burden would increase sluice line erosion and fill ash storage ponds more rapidly. Utilities which now sell fly ash for useful by-product (i.e. aggregate) would no longer have a uniform quality of ash with the dry injection process.

Dry limestone injection reduces precipitator efficiency, as mentioned earlier in this summary. Precipitators which could no longer meet pollution standards as a result of limestone injection could only be upgraded at great expense. Maintenance costs for precipitators would increase for reasons of wear.

On-site limestone preparation equipment would raise new operation and maintenance requirements. Some additional personnel would be required. Process application to a large plant would require several acres for preparation equipment and the limestone storage pile. The operation need not involve excessive dust formation but more dust would be created.

Process Economics

The major factors affecting process economics include (1) power unit size, (2) sulfur content of fuel, (3) stoichiometric rate of limestone injection, (4) particle size of injected limestone, (5) particulate removal requirements, (6) solids disposal needs, (7) raw material costs, (8) annual operating time, and (9) remaining life of the power unit. To evaluate the major factors, a variety of unit sizes, fuel sulfur levels, and limestone injection stoichiometries are chosen for case projections of fixed investment requirements, annual operating costs, and lifetime operating costs. Using selected cases, other key factors are also varied to analyze their sensitivity on process economics.

A 52-case parametric study, selected to expand the applicability of the Shawnee results over a broad range, is used to cover the various unit sizes, sulfur levels, and injection stoichiometries. The projections are based on existing power units utilizing pulverized coal, frontal-fired boilers with existing mechanical and electrostatic dust collectors in series. Costs for additional pond facilities for disposal of the injected solids are not included. In evaluating the results, it should be mentioned that the estimated investment requirements would be higher for power plants which require additional pond facilities for disposal of solids, or for systems with other combinations of existing dust collection facilities.

Investment—The estimated total fixed investment requirements for the dry limestone injection process are summarized in table 1 for each of the 52 cases established. These investments range from $751,500 ($15.0/kW) for a 50 MW - 0.8% S coal-fired unit with an injection stoichiometry of 3.0 to $5,645,500 ($16.1/kW) for a 350 MW - 5.0% S coal-fired unit with an injection stoichiometry of 4.0; however, unit investment costs vary from $5.8 to $36.8/kW depending upon power unit size, sulfur in coal, and injection stoichiometry.

The general relationship between power unit size, injection stoichiometry, and total dry limestone process investment is shown in figure 1 for installations utilizing 3.0% sulfur coal.

Annual operating cost—Based on an annual operation of 5,000 hours/year, projected operating costs, including regulated profit and income taxes, range from $298,400 ($3.05/ton coal burned) for a 50 MW - 0.8% S coal-fired unit with an injection stoichiometry of 3.0 to $4,122,700 ($5.85/ton coal burned) for a 350 MW - 5.0% S coal-fired unit with an injection stoichiometry of 4.0. Unit operating costs vary from $1.23 to $8.72/ton coal burned, or from 0.48 to 3.51 mills/kWh. Operating costs per ton of sulfur removed decrease with increasing power unit size and injection stoichiometry. These unit costs range from $316/ton sulfur removed for a 350 MW - 5.0% S coal-fired unit with an injection stoichiometry of 4.0 to $2,664/ton sulfur removed for a 50 MW - 0.8% S coal-fired unit with an injection stoichiometry of 3.0.

Table 1

Total Fixed Investment Requirements for Dry Limestone Injection Process Applied to Existing Power Units Equipped with Mechanical and Electrostatic Dust Collectors in Series[a]

Sulfur in coal %	Injection stoichiometry, moles CaO injected per mole sulfur in coal	Total fixed investment							
		50 MW units		150 MW units		250 MW units		350 MW units	
		$	$/kW	$	$/kW	$	$/kW	$	$/kW
0.8	3.0	751,500	15.0	1,280,100	8.5	1,695,100	6.8	2,032,300	5.8
0.8	4.0	834,500	16.7	1,431,500	9.5	1,868,100	7.5	2,278,800	6.5
0.8	5.0	908,300	18.2	1,568,800	10.5	2,086,100	8.3	2,503,200	7.2
0.8	6.0	975,000	19.5	1,694,400	11.3	2,253,600	9.0	2,707,700	7.7
0.8	7.0	1,036,300	20.7	1,808,000	12.1	2,407,700	9.6	2,893,300	8.3
3.0	1.0	817,100	16.3	1,404,600	9.4	1,865,600	7.5	2,238,600	6.4
3.0	2.0	1,070,500	21.4	1,874,200	12.5	2,498,900	10.0	3,005,900	8.6
3.0	3.0	1,271,500	25.4	2,251,400	15.0	3,011,400	12.0	3,676,800	10.5
3.0	4.0	1,442,000	28.8	2,574,200	17.2	3,498,000	14.0	4,262,100	12.2
5.0	1.0	995,300	19.9	1,736,200	11.6	2,314,500	9.3	2,782,700	8.0
5.0	2.0	1,332,900	26.7	2,369,500	15.8	3,221,100	12.9	3,927,000	11.2
5.0	3.0	1,602,600	32.1	2,926,600	19.5	3,968,400	15.9	4,766,400	13.6
5.0	4.0	1,838,700	36.8	3,376,200	22.5	4,582,000	18.3	5,645,500	16.1

[a] Fixed investment includes cost of additional electrostatic precipitator for reducing dust emission to same level obtained prior to installation of dry limestone injection process. Additional pond disposal area not included.

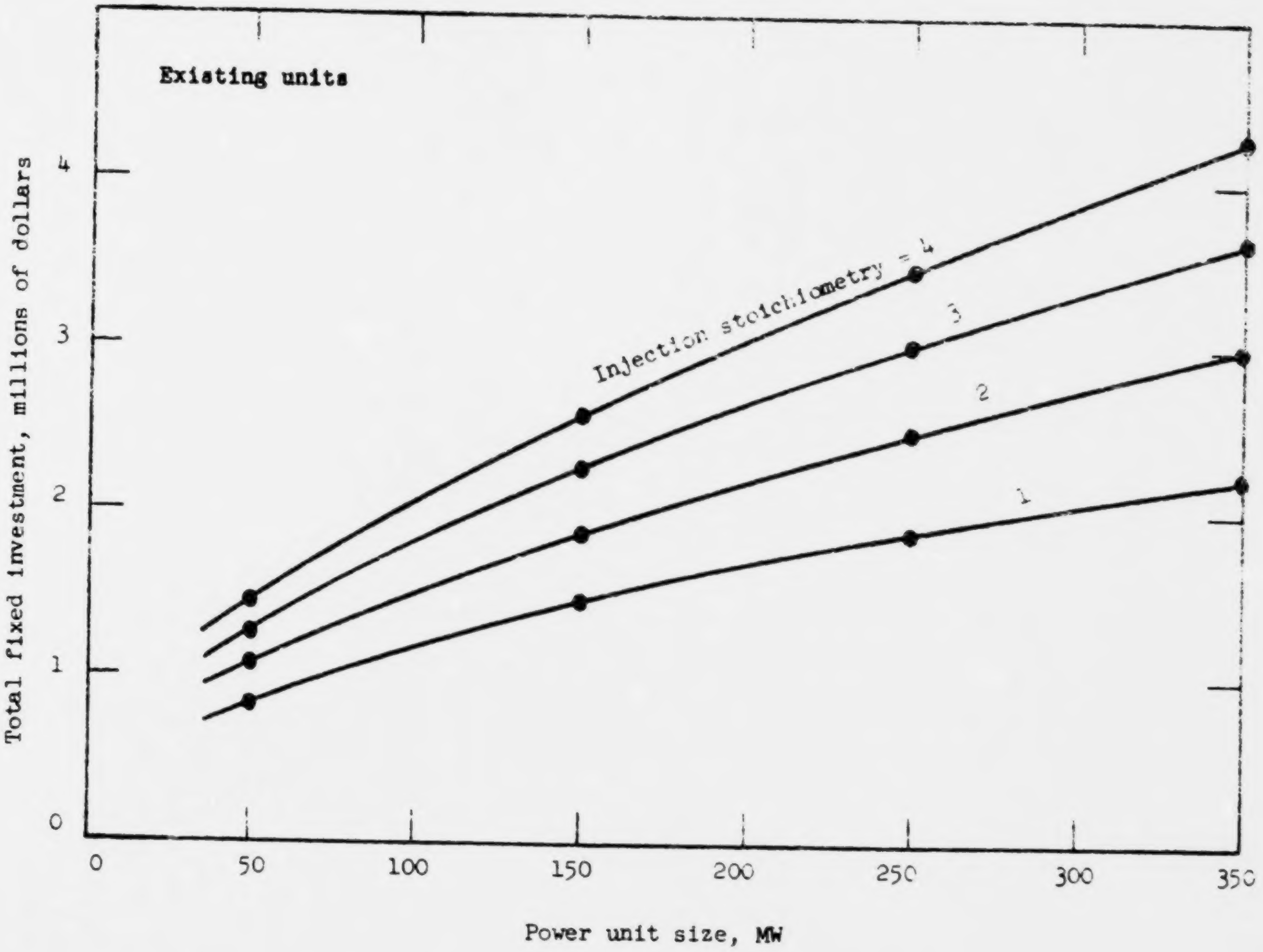

Figure 1 **Effect of Power Unit Size and Injection Stoichiometry on Total Dry Limestone Process Investment: 3.0% S Coal**

Table 2 shows the average annual operating cost for the various installations, assuming 3.0% sulfur coal. The general relationship between power unit size, injection stoichiometry, and annual operating cost are shown in figure 2.

Lifetime operating cost—Lifetime operating cost is based on a 15-year declining operating profile for the power plant. The following profile is assumed during the remaining years of operation:

Plant age, years	Plant remaining life, years	Annual operation, (on-stream time) hours at full generating capacity
16 - 20	15 - 11	5,000
21 - 25	10 - 6	3,500
26 - 30	5 - 1	1,500

Lifetime operating costs for the 52-case parametric study range from $3,909,400 (present worth = $2,223,900) for a 50 MW - 0.8% S coal-fired unit with an injection stoichiometry of 3.0 to $47,281,000 (present worth = $27,443,100) for a 350 MW - 5.0% S coal-fired unit with an injection stoichiometry of 4.0. Lifetime unit operating costs are somewhat higher than average annual operating costs due to the pronounced effect of the declining operating profile assumed for the power plant.

Lifetime results for the 3.0% sulfur coal installations are summarized in table 3, and shown graphically in figure 3.

The sensitivity of limestone particle size on investment and operating cost for three levels of grind at various throughput capacities was established. Results indicate that the investment required for grinding to 80% - 400 mesh is about 35-40% greater than that required for grinding to 80% - 200 mesh, and the higher grinding capability increases total process investment approximately 7-10%. Grinding operating costs are approximately 25-30% higher for the fine grind facilities; however, the effect of higher levels of grind on overall process costs is relatively small since grinding costs account for only 5-6% of the total operating cost.

Low sulfur coal installations appear to be the only installations for which the proposed EPA emission standards could practically be met by the dry limestone injection process. Although the total operating cost is likely to be lower, operating costs per ton of sulfur removed are notably higher for the low sulfur coal applications.

(See appendix L for full report.)

Table 2

Average Annual Operating Cost for Dry Limestone Injection Process Under Regulated Economics 3.0% Sulfur Coal[a]

Power unit size, MW	Injection stoichiometry, moles CaO injected per mole sulfur in coal	Average annual cost, $	Unit operating cost		
			$/ton coal	mills /kWh	$/ton S removal
50	1.0	323,100	3.30	1.29	1188
50	2.0	435,100	4.42	1.74	800
50	3.0	536,400	5.42	2.15	651
50	4.0	631,700	6.36	2.53	576
150	1.0	561,800	1.91	0.75	695
150	2.0	835,200	2.83	1.11	512
150	3.0	1,091,400	3.68	1.46	443
150	4.0	1,337,300	4.48	1.78	406
250	1.0	773,100	1.58	0.62	568
250	2.0	1,197,800	2.43	0.96	440
250	3.0	1,612,100	3.26	1.29	391
250	4.0	2,018,100	4.06	1.61	368
350	1.0	965,900	1.41	0.55	507
350	2.0	1,547,400	2.25	0.88	406
350	3.0	2,120,500	3.06	1.21	368
350	4.0	2,667,100	3.83	1.52	348

[a] Existing units - 15 yrs. remaining life
5000 hrs. operation/yr

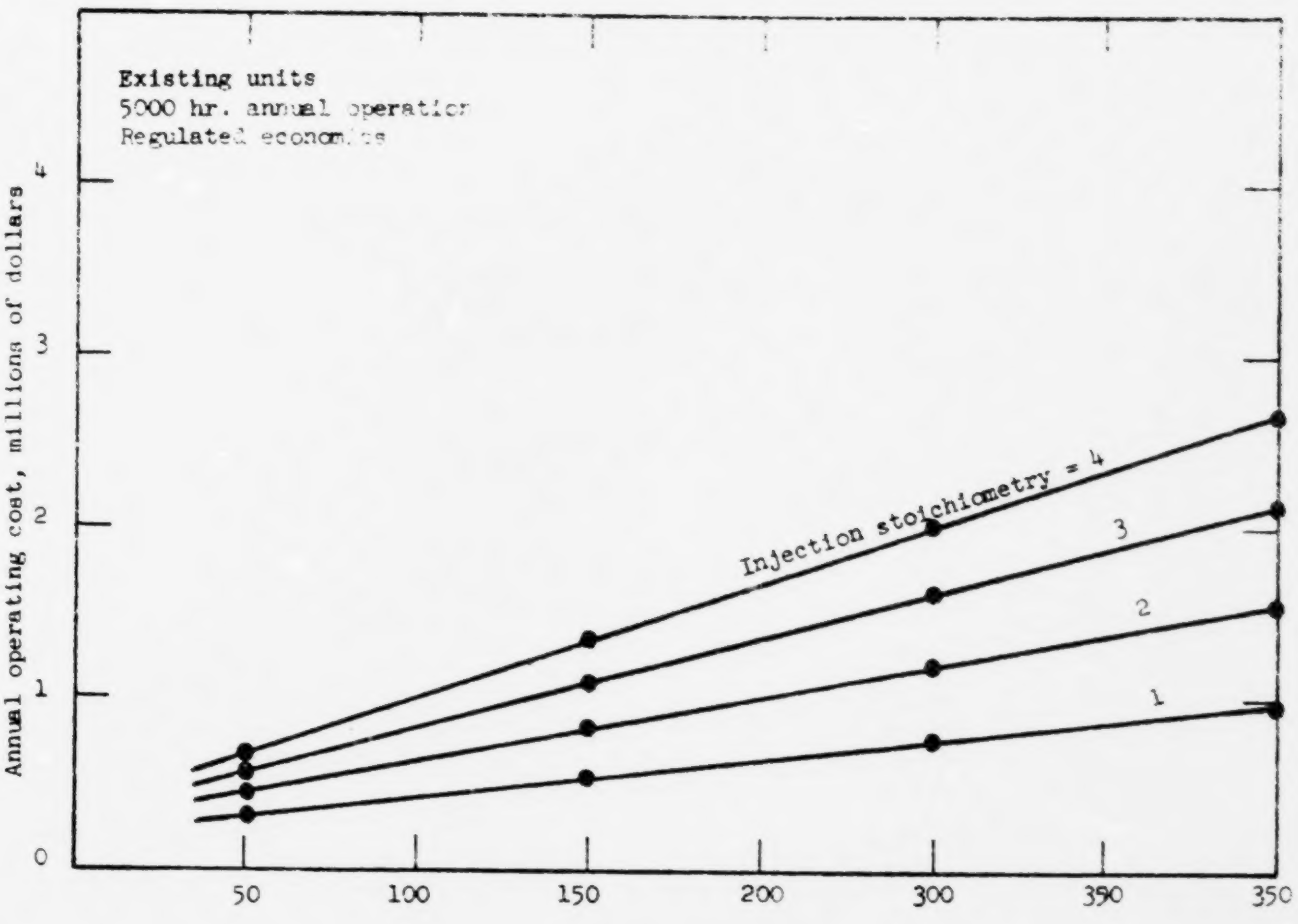

Figure 2 Effect of Power Unit Size and Injection Stoichiometry on Annual Operating Cost of Dry Limestone Process: 3.0% S Coal

Table 3

Lifetime Operating Cost for Dry Limestone Injection Process Under Regulated Economics 3.0% Sulfur Coal[a]

Power unit size, MW	Injection stoichiometry, moles CaO injected per mole sulfur in coal	Lifetime operating cost (net increase in cost of Power)				Cumulative present worth of net increase in cost of power, discounted at 10%/yr			
		$	$/ton coal	mills/kWh	$/ton S removed	$	$/ton coal	mills/kWh	$/ton S removed
50	1.0	4,227,100	4.31	1.69	1554	2,406,900	2.46	0.96	885
50	2.0	5,607,200	5.70	2.24	1031	3,205,200	3.26	1.28	589
50	3.0	6,826,500	6.90	2.73	828	3,911,300	3.95	1.56	475
50	4.0	7,955,200	8.00	3.18	726	4,565,900	4.59	1.83	417
150	1.0	7,220,700	2.46	0.96	894	4,135,700	1.41	0.55	512
150	2.0	10,438,200	3.53	1.39	640	6,002,800	2.03	0.80	368
150	3.0	13,388,600	4.51	1.79	543	7,717,400	2.60	1.03	313
150	4.0	16,181,700	5.43	2.16	491	9,342,200	3.13	1.25	283
250	1.0	9,808,700	2.00	0.78	721	5,633,500	1.15	0.45	414
250	2.0	14,708,000	2.99	1.18	541	8,480,000	1.72	0.68	312
250	3.0	19,404,000	3.92	1.55	471	11,207,900	2.27	0.90	272
250	4.0	23,965,700	4.82	1.92	437	13,863,600	2.79	1.11	253
350	1.0	12,121,000	1.77	0.69	637	6,973,000	1.02	0.40	366
350	2.0	18,751,600	2.72	1.07	492	10,824,500	1.57	0.62	284
350	3.0	25,199,100	3.64	1.44	437	14,573,700	2.10	0.83	253
350	4.0	31,268,000	4.49	1.79	408	18,110,200	2.60	1.03	236

a. Existing units - 15 yrs. remaining life. Assumed operating profile: 5 yr @ 5000 hr/yr
5 yr @ 3500 hr/yr
5 yr @ 1500 hr/yr

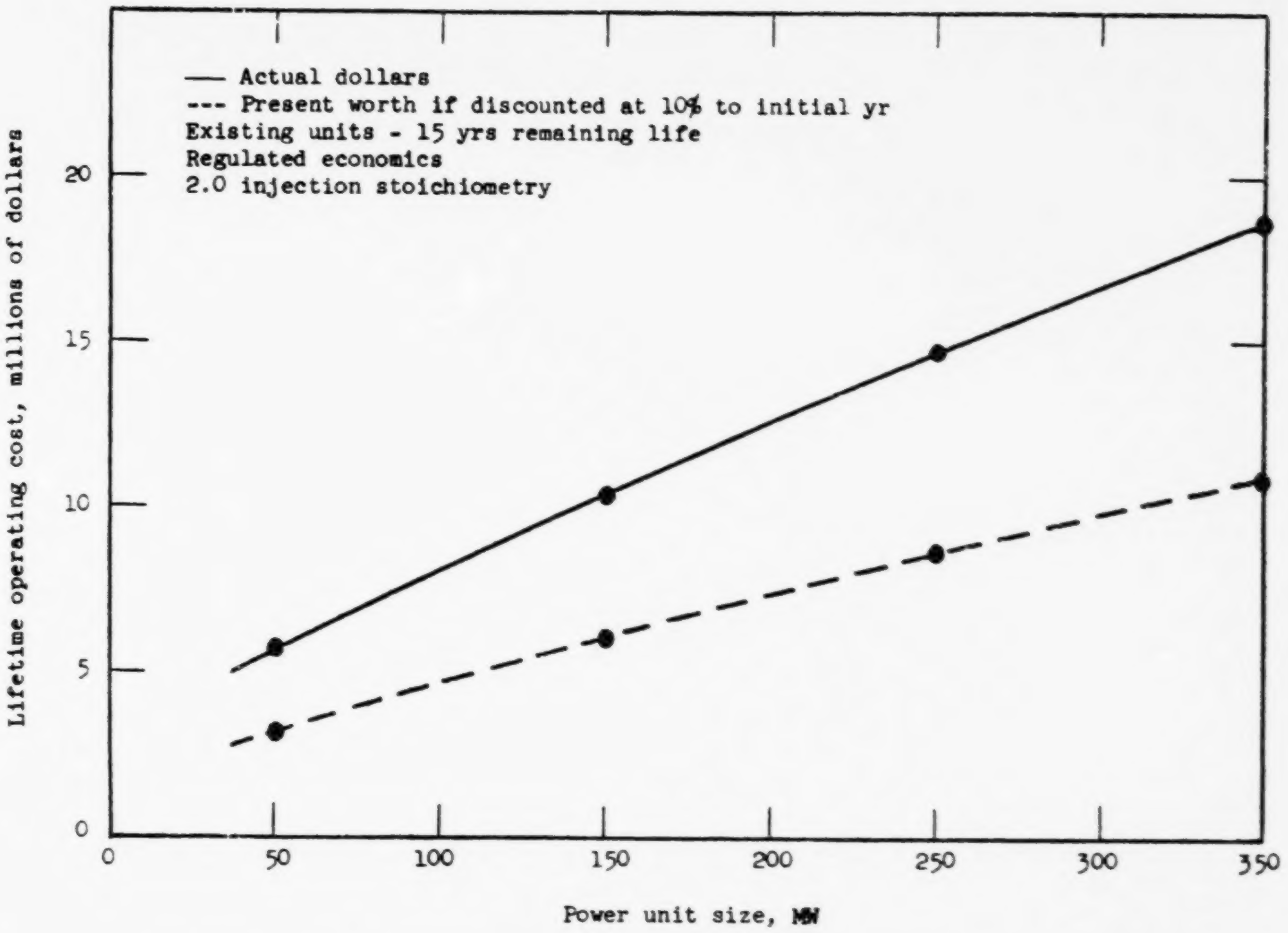

Figure 3 Effect of Power Unit Size and Injection Stoichiometry on Lifetime Increase in Cost of Power Using Dry Limestone Injection: 3.0% S Coal

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INTRODUCTION

Background

The electric utility industry is faced with the problem of reducing sulfur dioxide and particulate emissions from coal and oil-fired steam generating plants. In the 1960's, research effort was beginning on several methods which could ultimately reduce these pollutants and yield either a waste product or one of potential reuse. Based on process simplicity, apparent low cost and existing knowledge, a logical approach was to choose dry limestone injection as a first generation process for full-scale demonstration. Research in the United States and overseas had shown that the gas-solid reaction between calcined limestone, CaO, and SO_2 would reduce the pollutant SO_2 but obviously at the added expense of raising dust emissions for which suitable removal devices exist. The time had arrived when comprehensive full-scale demonstration testing of the process was justified to obtain answers on removal effectiveness and reveal more of those factors that make-or-break most endeavors.

The Environmental Protection Agency and Tennessee Valley Authority began a cooperative effort funded by EPA and conducted on a 150-mw boiler at Shawnee Steam Plant. Numerous technical support contracts were undertaken by EPA to assist in the full-scale evaluation. Particular emphasis was applied to process modeling and limestone factors such as particle properties, availability of limestone and possible use of the large tonnages of limestone modified fly ash that would be available if wide spread use developed for the process. Hopefully, some cost data from actual operating conditions would become available but brevity of the long term injection period reduced the significance of this data. However, an extensive economic analysis was made of units 50 to 350 mw in size and burning coals with 0.8%, 3%, and 5% sulfur. Particular attention focused on sluice water since the higher ash burdens containing calcium sulfate and unreacted lime would possibly alter ionic content of the ash sluice pond.

This report attempts to summarize what was learned by conducting this extensive program. Complete details of individual activities are available in EPA reports on work performed in-house and by its contractors. At an early date, the Control Systems Division of EPA selected the dry limestone injection process for development and full-scale demonstration. Several years later this approach was supported by the National Academy of Engineering[1] *, which recommended on the highest priority basis the development of "throw-away" processes (those not yielding a marketable by-product) for SO_2 control. Sufficient work had been done to suggest this type may be commercially acceptable sooner than those which produce salable products and that their net cost may be less than recovery processes.

Of the processes that have been proposed, injection of limestone into the boiler is the simplest and requires the least investment. For this reason, despite relatively low SO_2

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*Superscripts refer to References in main text.

removal, the process was considered to have potential for applicability to older and small-to-medium size power plants having limited remaining life and for which the more efficient but more expensive processes would be economically unfeasible. Intermittent operation seemingly made the process suitable for plants with low load factors. Dry limestone injection has the possibility for SO_2 episode control and even shutdown of injection under favorable atmospheric conditions.

The Chemical Process

The basic concept of the process is very simple—pulverized limestone ($CaCO_3$) is injected into the combustion chamber of the boiler where it flash calcines to lime (CaO) and at the same time begins to react with sulfur dioxide (SO_2) and oxygen (O_2) to form calcium sulfite ($CaSO_3$) and/or calcium sulfate ($CaSO_4$) according to the following equations:

$$CaCO_3 \longrightarrow CaO + CO_2 \text{ (calcination)}$$

$$CaO + SO_2 \longrightarrow CaSO_3 \text{ (sulfite formation)}$$

$$4CaSO_3 \longrightarrow 3CaSO_4 + CaS \text{ (sulfite disproportionation)}$$

$$CaS + 2O_2 \longrightarrow CaSO_4 \text{ (sulfation)}$$

$$CaO + SO_2 + 1/2\ SO_2 \longrightarrow CaSO_4 \text{ (sulfation)}$$

Magnesium carbonate ($MgCO_3$), a major component of dolomitic limestone, reacts in the same manner except at somewhat different temperatures. However, magnesium constituents have been found essentially unreactive with SO_2 under injection conditions. The thermodynamics of the $CaO\text{-}SO_2\text{-}O_2$ reaction are favorable; however, restrictions imposed on the reaction by the system make it difficult to attain a reasonable level of efficiency.

The process involves injection of pulverized limestone into the furnace where in the time interval of about one second, flash calcination, mixing and reaction with SO_2 occur. All this must be accomplished in a system consisting of turbulent combustion gases at temperatures up to 3,000° F moving out of the combustion zone at velocities exceeding 60 feet per second. Limestone is injected into the high temperature region of the furnace in order to calcine as rapidly as possible. The calcination reaction is endothermic, and the material remains relatively cool until CO_2 is driven off. Fundamental studies[24] of the reaction have shown that during this time CaO particles react with SO_2 to form $CaSO_3$ simultaneously with CO_2 evolution. As calcination nears completion and the particle temperature rises, the thermodynamic stability limit is exceeded and some $CaSO_3$ disproportionates. By this time the combustion gases are beginning to cool and the particle temperature goes through a maximum and then begins to decrease. This is the time when reaction with SO_2 is at a maximum. In this region the particle combines with SO_2 and O_2 to form $CaSO_4$ until the temperature decreases to about 1,700° F; then the reaction becomes so slow that it essentially ceases. Particles exposed to high temperature for excessive periods lose much of their chemical reactivity and become what is commonly termed "deadburned." If the particles are exposed to the proper time/temperature relationship, an active particle will result.

Previous Investigations

The attractive features of dry injection mentioned above resulted in extensive study of the process in Germany, Japan, Poland, Czechoslovakia, and in the United States. Table 1 lists these Pilot and Bench Scale Investigations. Despite the fact that these investigations were conducted under experimental conditions involving different furnace and reactor types, additive type, injection variables, and operating conditions there is considerable agreement in the results obtained.

Parameters affecting the sorption efficiency of injected limestone were shown to be (1) properties of the limestone that affected degree of porosity after calcination, (2) particle size and surface area, (3) temperature at point of injection, (4) retention time, (5) limestone distribution, (6) mass transfer between SO_2 in flue gas and sorbent particle, (7) SO_2 concentration, (8) furnace operating conditions, and (9) limestone feed rate.

Results generally agreed that percent stoichiometry, percent excess air and particle size have a positive correlation with SO_2 removal from a gas stream and suggested 1900° F to 2100° F as a good injection point temperature range. No significant differences were shown between injection of ground limestone, dolomite and hydrated dolomite. Although hydrated stones (particularly hydrated lime) were slightly more effective than their parent raw materials, the difference would not justify the process cost increment. In most cases, precalcination had a negative effect on SO_2 removal effectiveness. Catalysts were found to be ineffective.

Plant-scale tests of the process were also conducted in the United States and overseas during the 1960's. Without exception, full-scale results on oil fired units indicated higher than normal solids deposition on heat transfer surfaces. Full-scale results on coal fired units were inconclusive in this regard. Figure 1 is a plot of SO_2 Removal vs. Stoichiometry as reported for these pilot and bench scale tests. Plant scale SO_2 removal results are summarized in the curves of Figures 2 and 3.

Details of previous investigations are not included in this report but may be found in the references to the main text and/or in the appropriate appendix.

Despite the early investigations, information gaps existed which precluded confident assessment and utilization of the process. Lacking information included (1) the physical and chemical characteristics of good additives for SO_2 absorption, (2) the effect of additive distribution in the furnace on SO_2 removal, (3) the effect of injection temperature and boiler residence time on SO_2 removal, (4) the effect of the process on the boiler and overall system, and (5) the effect of unit operating conditions on the process.

The EPA Program

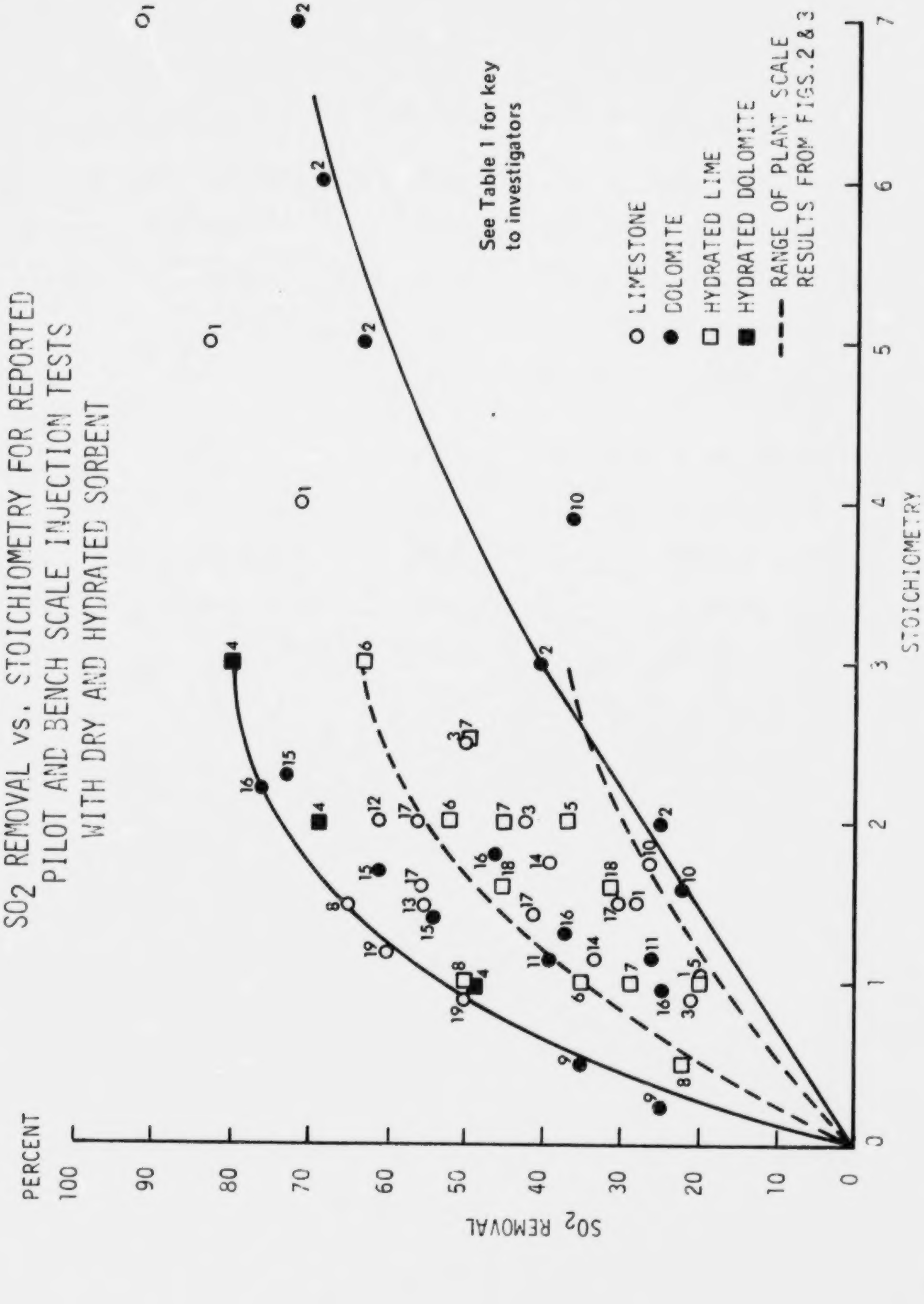
The prior investigation results and need for additional information were major reasons for the EPA to initiate in-depth evaluation of the Dry Limestone Injection Process. The approach taken was to study all the major variables on a broad front using in-house facilities, outside contractors and consultants, universities and other government agencies.

TABLE 1

PILOT AND BENCH SCALE INVESTIGATIONS OF THE DRY LIMESTONE PROCESS

Key Number for Fig. 1	Investigator	Scale	Fuel	Sorbent
1	TVA	Pilot	Coal (Sim. Gas)	Limestone
2	TVA	Pilot	Coal (Sim. Gas)	Dolomite
3	TVA	Pilot	Coal (Sim. Gas)	Limestone
4	Bergbau Forschung	Bench	Coal	Hydrated Dol.
5	Japan Resources Research Institute	Pilot	Oil	Hydrated Lime
6	Japan Resources Research Institute	Pilot	Oil	Hydrated Lime
7	Japan Resources Research Institute	Pilot	Oil	Hydrated Lime
8	Peabody Coal	Pilot	Coal	Limestone
9	Peabody Coal	Pilot	Coal	Dolomite
10	Babcock & Wilcox	Pilot	Coal	Dolomite
11	Peabody Coal	Pilot	Coal	Dolomite
12	Peabody Coal	Pilot	Coal	Limestone
13	Peabody Coal	Pilot	Coal	Limestone
14	Babcock & Wilcox	Pilot	Coal	Limestone
15	Poland	Pilot	Coal	Dolomite
16	Poland	Pilot	Coal	Dolomite
17	Czechoslovakia	Pilot	Coal	Limestone
18	Czechoslovakia	Pilot	Coal	Hydrated Lime
19	Ketov	Bench	Coal	Limestone

FIGURE 1



SO2 REMOVAL vs. STOICHIOMETRY FOR REPORTED PILOT AND BENCH SCALE INJECTION TESTS WITH DRY AND HYDRATED SORBENT

FIGURE 2

SO_2 REMOVAL vs. STOICHIOMETRY FOR REPORTED PLANT-SCALE TESTS OF DRY LIMESTONE INJECTION PROCESS

KEY	INVESTIGATOR	FUEL	SORBENT	FLUE GAS TEMP. °F AVG. AT INJECTION PT.
1	WISCONSIN ELECTRIC CO.	COAL	GROUND DOLOMITE	~3000
2	DETROIT EDISON CO.	COAL	GROUND DOLOMITE	~2800
3	STEAG (W.Germany)	COAL	GROUND LIMESTONE	2400
4	KANSAS POWER & LIGHT(C-E,Inc)	COAL	LIMESTONE	2100
5	UNION ELECTRIC CO(C-E,Inc)	COAL	DOLOMITE	2100
6	ENERGOPOMIAR (Poland)	COAL & GAS	DOLOMITE	2100
7	CENTRAL RESEARCH INSTITUTE OF ELECTRIC POWER (Japan)	OIL	LIMESTONE	2100
8	REPUBLIC COAL & COKE	COAL	DOLOMITE	2300
9	REPUBLIC COAL & COKE	COAL	DOLOMITE	2800
10	GENERAL MOTORS	COAL	DOLOMITE	1900
11	GENERAL MOTORS	COAL	LIMESTONE	1900

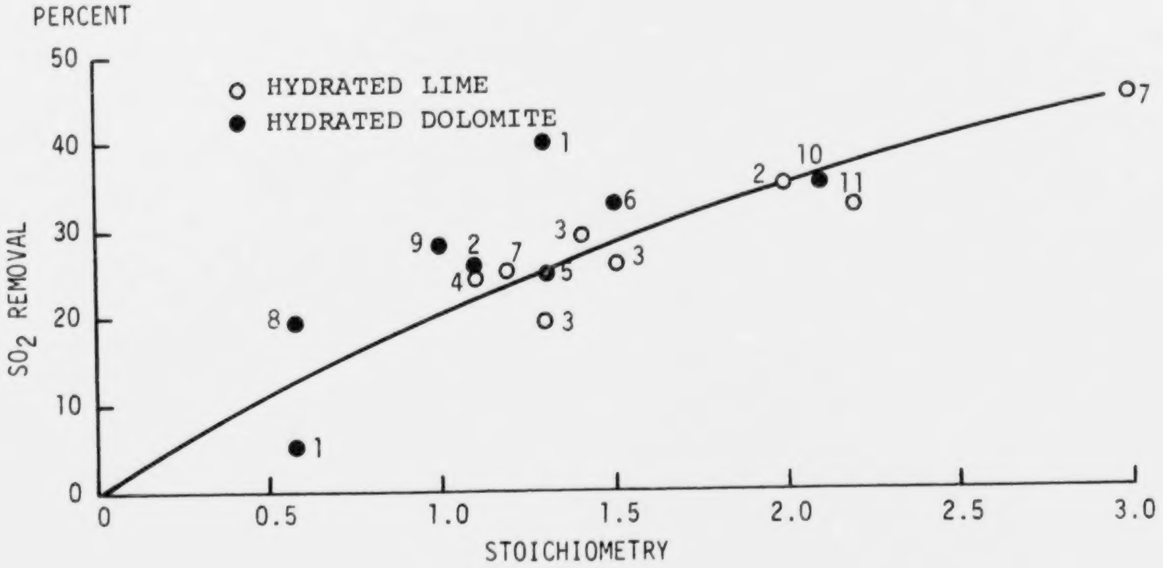
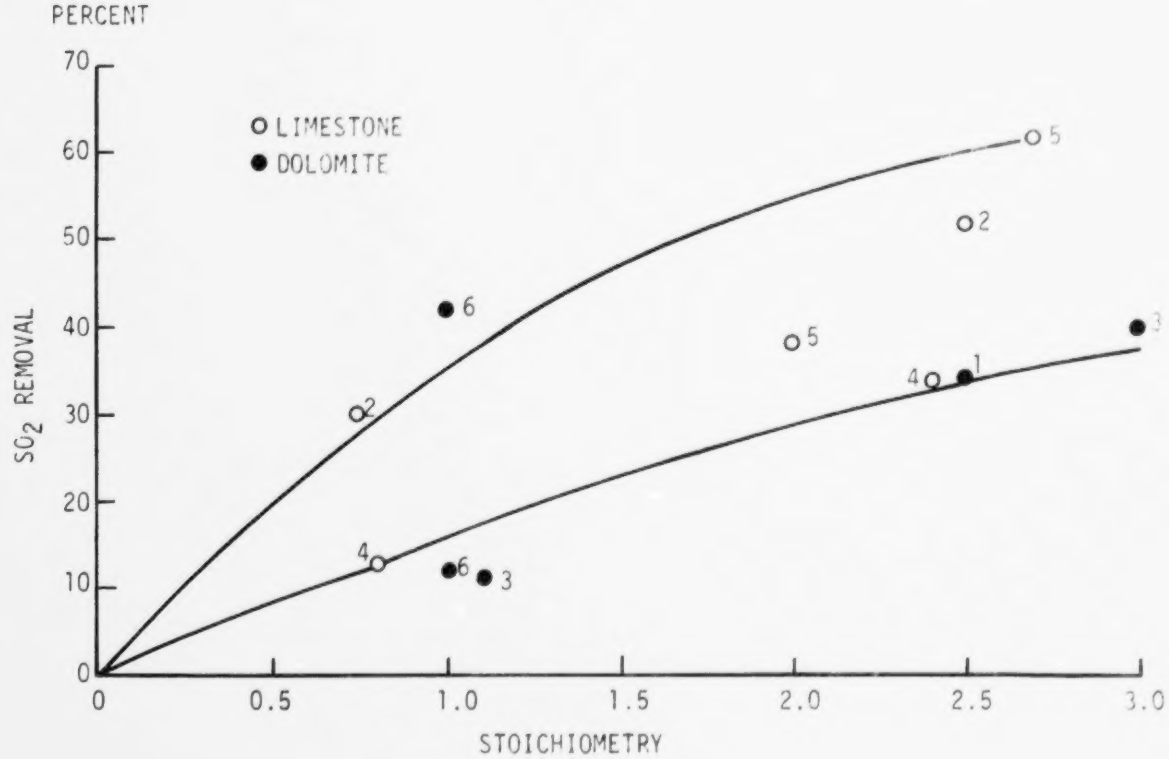


FIGURE 3

SO_2 REMOVAL vs. STOICHIOMETRY FOR REPORTED PLANT-SCALE INJECTION TESTS WITH HYDRATED LIME AND DOLOMITE

KEY	INVESTIGATOR	FUEL	SORBENT	FLUE GAS TEMP. °F AVG. AT INJECTION POINT
1	STEAG (W.Germany)	COAL	HYDRATED DOLOMITE	2100
2	TECHNICAL UNIVERSITY OF STUTTGART (W.Germany)	COAL & OIL	HYDRATED LIME	1830
3	TECHNICAL UNIVERSITY OF STUTTGART	COAL & OIL	HYDRATED DOLOMITE	1830
4	STEAG	COAL	HYDRATED LIME	2100
5	CENTRAL RESEARCH INST. OF ELECTRIC POWER (Japan)	COAL	HYDRATED LIME	2100
6	MOBIL OIL AG. (W.Germany)	OIL	HYDRATED DOLOMITE	2500



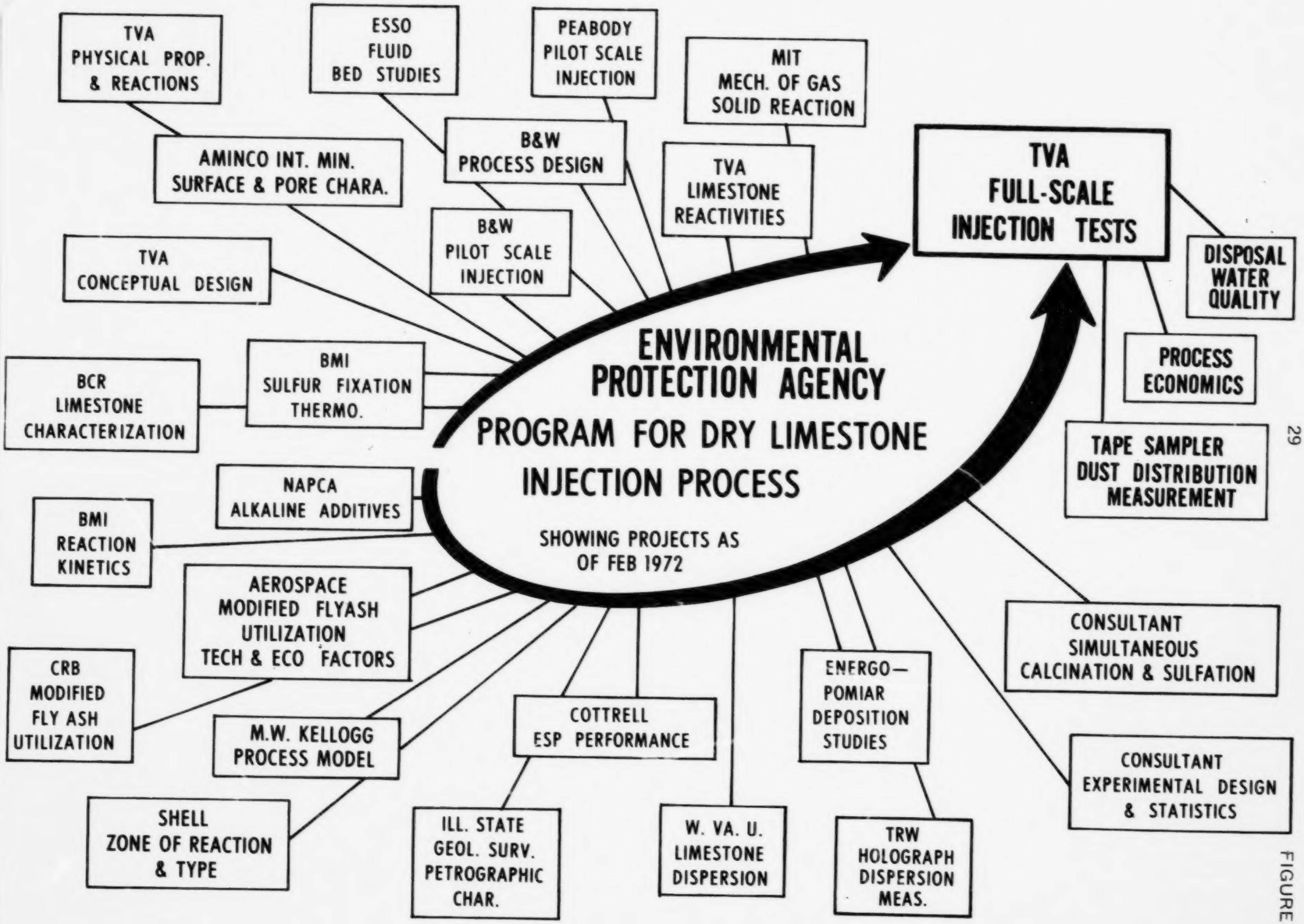
Initial effort was through a letter agreement with the TVA. A conceptual design study (Ref. 2) was initiated in late 1967 followed by detailed process design and construction of limestone handling and injection equipment for installation on a 150-MW pulverized coal-fired boiler at the Shawnee Steam Plant, Paducah, Kentucky, in 1969 and 1970. Equipment shakedown and system operation began in mid-1970 and was followed by process optimization and trials at long term operation. The general objectives of this program were to optimize the process and to develop operating and economic data for process utilization.

Major activities in support of the full-scale project were primarily in the areas of:

1. Fundamental studies on reaction rates and properties of limestone and effects of limestone characteristics.
2. Development of simulation models including limestone penetration and dispersion, calcination, sulfation, and simultaneous calcination and sulfation.
3. Effects of injected limestone on solids collection equipment and on waste water quality.
4. Utilization of limestone modified fly ash.

Figure 4 shows the organizations involved and the activities they carried out in the overall program.

FIGURE 4


ENVIRONMENTAL PROTECTION AGENCY
PROGRAM FOR DRY LIMESTONE INJECTION PROCESS
SHOWING PROJECTS AS OF FEB 1972
TVA FULL-SCALE INJECTION TESTS
DISPOSAL WATER QUALITY
PROCESS ECONOMICS
TAPE SAMPLER DUST DISTRIBUTION MEASUREMENT
CONSULTANT SIMULTANEOUS CALCINATION & SULFATION
CONSULTANT EXPERIMENTAL DESIGN & STATISTICS
TRW HOLOGRAPH DISPERSION MEAS.
ENERGO—POMIAR DEPOSITION STUDIES
W. VA. U. LIMESTONE DISPERSION
COTTRELL ESP PERFORMANCE
ILL. STATE GEOL. SURV. PETROGRAPHIC CHAR.
SHELL ZONE OF REACTION & TYPE
M.W. KELLOGG PROCESS MODEL
CRB MODIFIED FLY ASH UTILIZATION
AEROSPACE MODIFIED FLYASH UTILIZATION TECH & ECO FACTORS
BMI REACTION KINETICS
NAPCA ALKALINE ADDITIVES
BCR LIMESTONE CHARACTERIZATION
BMI SULFUR FIXATION THERMO.
TVA CONCEPTUAL DESIGN
AMINCO INT. MIN. SURFACE & PORE CHARA.
TVA PHYSICAL PROP. & REACTIONS
ESSO FLUID BED STUDIES
B&W PROCESS DESIGN
B&W PILOT SCALE INJECTION
PEABODY PILOT SCALE INJECTION
MIT MECH. OF GAS SOLID REACTION
TVA LIMESTONE REACTIVITIES

TEST PROGRAM

I. OBJECTIVES AND OVERALL APPROACH

The objectives of the full-scale injection test program as developed during discussion between NAPCA (forerunner of EPA) and TVA in 1969 were to:

1. Provide a system to distribute limestone in the gas stream to ensure maximum exposure of the additive particles to their proportional amount of sulfur dioxide.
2. Optimize sulfur dioxide removal with representative limestones and coal supplies by utilizing information from all support studies.
3. Determine effect of limestone injection on plant operation during extended operating periods.
4. Obtain information that would permit application of the process to other boiler types with no further research and development required.
5. Obtain cost information to upgrade previous estimates.

The approach to accomplish these objectives was division of activity into four phases which were designated:

Phase I	Shakedown
Phase II	Dust Distribution
Phase III	Process Optimization
Phase IV	Long-term Operation

Outside contractors, consultants, universities, and others were retained to apply their expertise in particular technical areas. Their contributions are integrated and discussed in context with results and conclusions of the full-scale Shawnee work. Details of their individual activities are given in appendices.

Calcined limestone must be distributed properly in the reaction zone of the furnace if effective SO_2 removal is to occur. The test program was designed such that following equipment shakedown, the first series of tests would be directed toward optimization of limestone distribution. It was expected that preliminary information gathered during shakedown tests would provide helpful indicators of sulfur dioxide removal sensitivity to particle size, temperature environment, excess air, sulfur in coal, injection system variables, and stoichiometery. Knowledge of these would be helpful in carrying out the process optimization phase whose results, in turn, would be applied to the long-term operation.

Accomplishment of the above objectives required construction of considerable equipment outside the powerhouse in addition to some inside along with providing injection ports into Unit 10. A description of this test facility follows.

II. TEST FACILITY

A. UNIT 10 BOILER

Selection of Shawnee Unit 10 was based on its size and type firing, being representative of boilers that are potential users of the process. Unit 10 is located at the end of the powerhouse and is closest to the site where stone preparation equipment is erected. It is a pulverized-coal, front-fired boiler designed by Babcock & Wilcox to produce 1,000,000 pounds of steam an hour at 1,800 psig and 1,000 °F superheat with reheat to 1,000 °F. The unit is normally operated at 150 MW and has a peaking capacity of 175 MW. Full load coal consumption is approximately 60 tons an hour. Firing equipment consists of 16 front wall circular burners served by four pulverizers. The unit is equipped with 65% efficient mechanical fly ash collectors followed by 90% efficient electrostatic precipitators which result in an overall ash collection efficiency of 96%.

The unit is fired with coal containing an average of 15% ash and 2.7% sulfur. Combustion of this fuel produces flue gas containing about 3.5 grains of fly ash per standard cubic foot of gas with an SO_2 concentration of 2,200 ppm by volume.

Figure 5 is a sectional elevation of the unit. Additional statistics on the boiler and limestone system are found in appendix A. The only boiler modifications required for the test program were installation of bent tube panels into water wall locations where injection nozzles and sampling probes penetrated. A small panel (17" by 21") was added in the control room for operating limestone feeders. Divided coal bunkers allowed control of coal supply as tests required.

B. LIMESTONE INJECTION PROCESS EQUIPMENT

Equipment design was dictated for the most part by the objectives of the program which required that limestone of the proper size be injected into the boiler furnace at locations which would assure optimum distribution and maximum retention time in the appropriate temperature zone. Flexibility in the system to study these variables was also a requirement. Based on the above considerations, system design criteria were specified.

The Babcock & Wilcox Company designed the limestone preparation and injection system which was erected by TVA's Construction Services Branch. These two major parts of the system will now be described in detail.

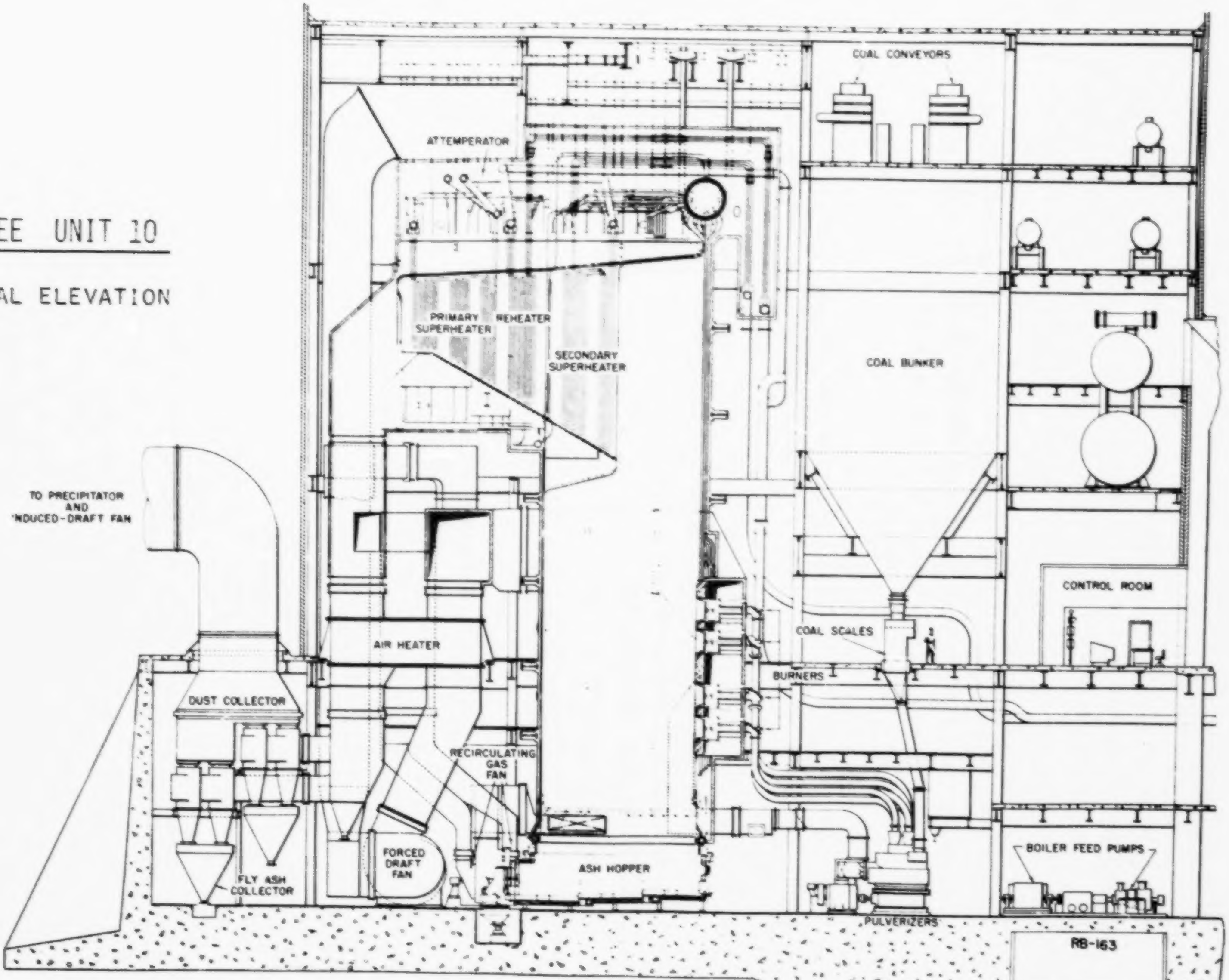
1. Limestone Receiving and Preparation System

The entire preparation system is shown in Figure 6 on the left half. A storage area capable of holding 10,000 tons of raw limestone and located adjacent to a railroad unloading area was equipped with a stocking out conveyor. The system was designed for operating flexibility to thoroughly investigate the process. The system can receive raw limestone by truck or rail and then pulverize it to a fineness of from 70% to 95% through 325 mesh before injection into the furnace. In operation the raw limestone from the receiving hopper was conveyed and metered by a volumetric feeder to an oil-fired rotary dryer where moisture was reduced to less than a half percent to facilitate pulverization in the ball mill. Dried stone leaving the drier was moved by a bucket

FIGURE 5

SHAWNEE UNIT 10

SECTIONAL ELEVATION


COAL CONVEYORS
ATTEMPERATOR
PRIMARY SUPERHEATER
REHEATER
SECONDARY SUPERHEATER
COAL BUNKER
TO PRECIPITATOR AND INDUCED-DRAFT FAN
CONTROL ROOM
COAL SCALES
AIR HEATER
BURNERS
DUST COLLECTOR
RECIRCULATING GAS FAN
FORCED DRAFT FAN
FLY ASH COLLECTOR
ASH HOPPER
BOILER FEED PUMPS
PULVERIZERS
RB-163

elevator to a surge tank that served as a feedbin for the ball mill. A volumetric feeder which operates on signal derived by sound pickup from the mill delivered stone to the mill inlet. Figure 7 shows the general arrangement of the mill and classifier. Air circulated past the mill discharge at sub-atmospheric pressure carried pulverized stone to a gyrotor classifier where oversize stone was diverted to the mill inlet and product went to a cyclone separator for gravity discharge into the storage tank. A pump under this tank provided pneumatic transport of pulverized limestone into a smaller feed tank located adjacent to Unit 10 inside the powerhouse.

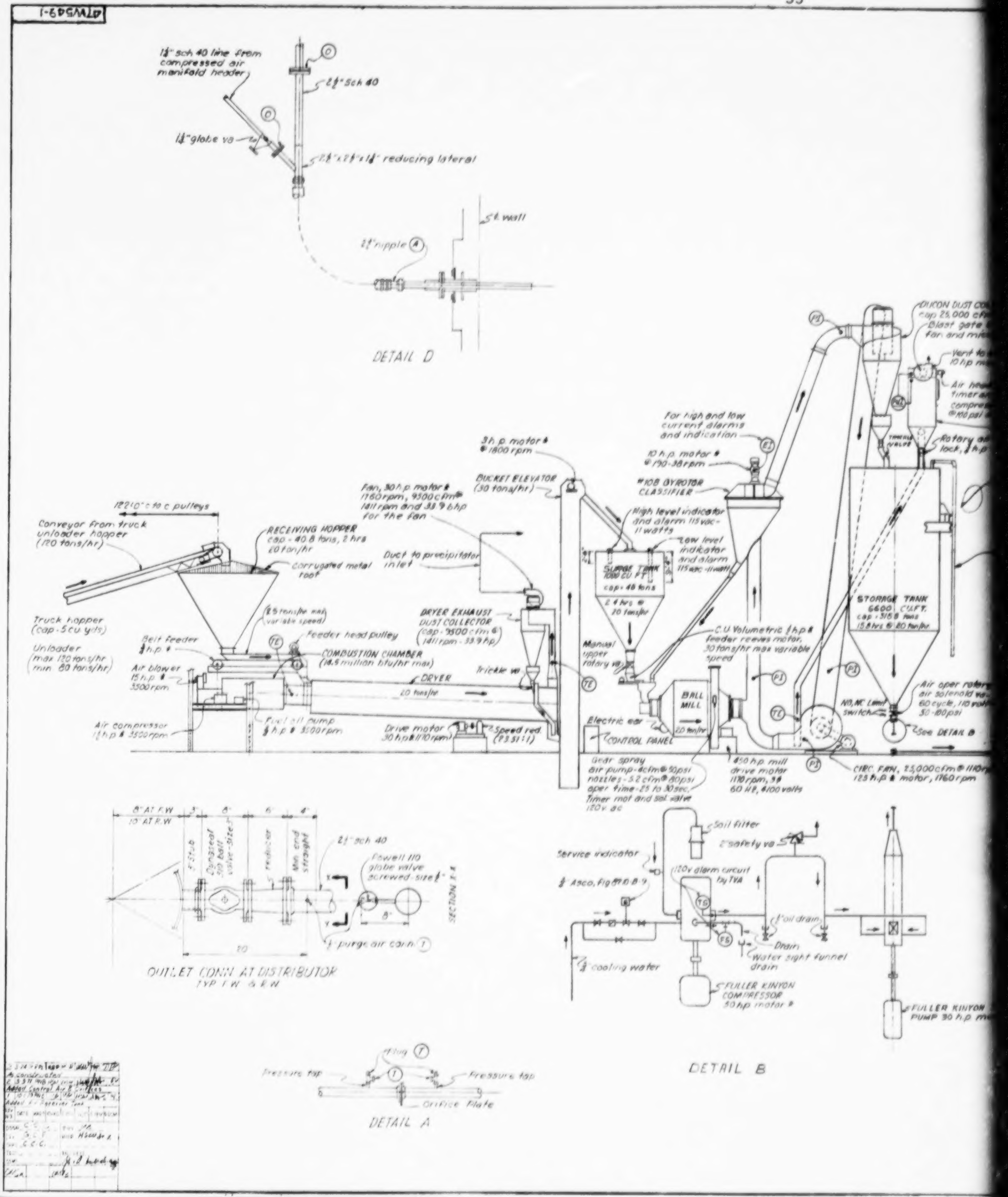
Design factors had to account for possible wide variations in raw stone moisture and variations in mill capacity as a function of desired product particle size.

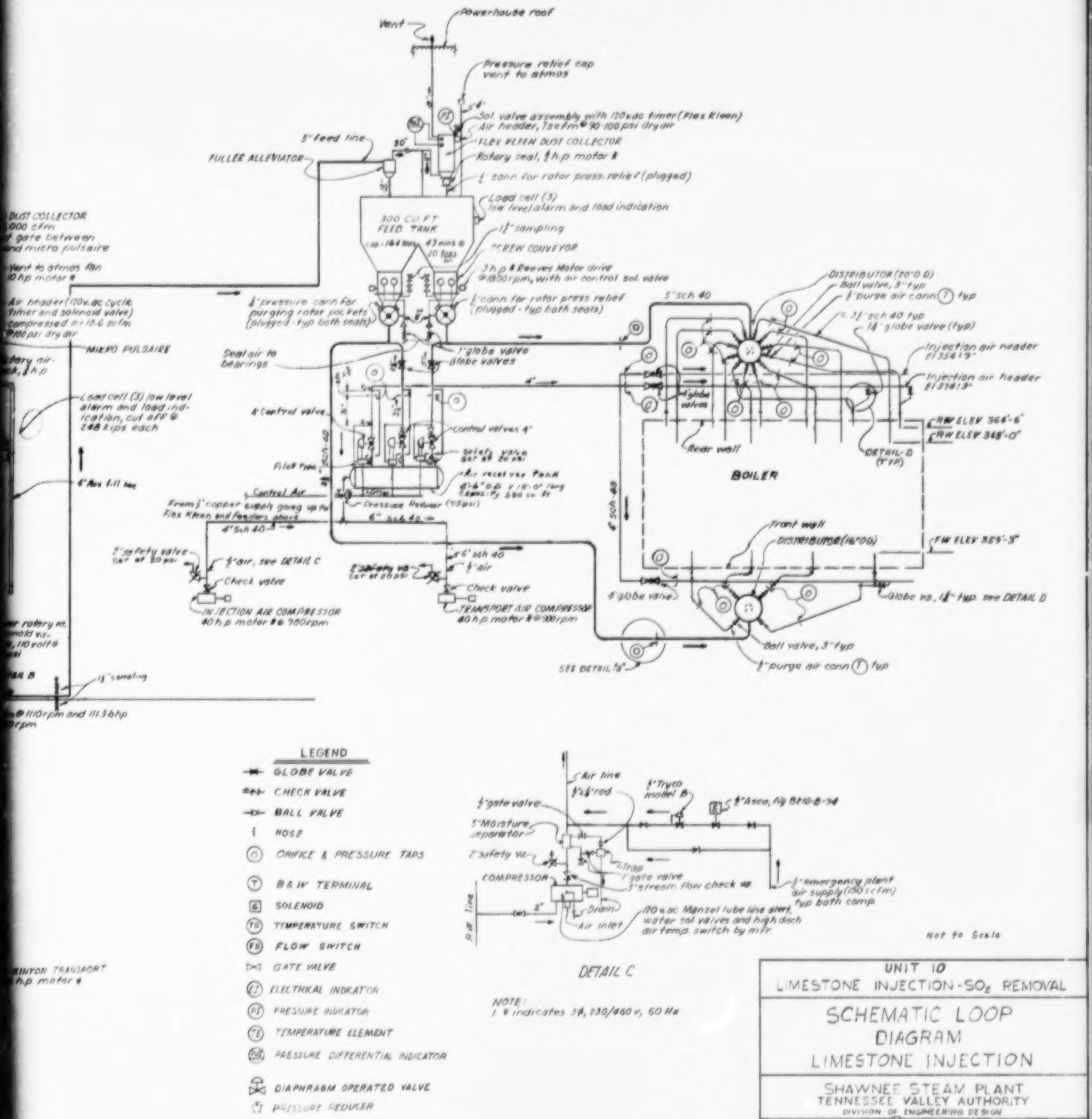
2. Limestone Injection System

A schematic of the injection system is shown on the right half of Figure 6. The variable screw conveyor and rotary feeder metered limestone from the feed tank to an air transport system. The rotary feeder was controlled manually at a local point or automatically from unit 10 control room. The air transport system conveyed the pulverized product through a distributor can and into the boiler furnace. Figure 8 shows this distributor can located at the upper rear elevation of the boiler. Individual transport pipes conducted the pulverized limestone to individual injection nozzles at the upper and lower rear sites, typically shown in Figure 9. A smaller but separate distributor served four front nozzles.

Limestone is distributed into the furnace gas stream by use of injection nozzles spaced across the width of the furnace at three different elevations. There are two rows of six injectors each on the rear wall opposing the burners and one row of four injectors on the front wall of the furnace just above the top row of burners. Elevations of these injection sites are shown in Figure 10. Based on draft limitations in the boiler, Babcock & Wilcox Company recommended dense phase transport and injection of pulverized limestone with air. The number and size of injection nozzles at two elevations on the rear wall were based on their experience with addition of tempering air to a boiler. In addition to the two primary elevations, the third set of four nozzles was recommended for location on the front wall above the burners and between the high and low elevations. It was assumed that the rear wall injectors might not provide deep enough penetration to get limestone distribution completely across the boiler and that the front injectors would also be required to inject material into a turbulent region above the burners and thereby improve coverage of the area along the front wall. Operation with simultaneous front and rear injection later proved difficult to control and required a piping modification. This is covered under the section on System Operating Reliability.

Transport air picks up limestone at the rotary feeder and carries it to the distributor can at the front or rear, depending on the injection site. Passing vertically upward along the can centerline the flow is divided equally to individual injection lines sized for 3,000 feet per minute flow velocity. The injection nozzles were constructed of 2-1/2 inch, heavy wall, type 316 stainless steel.


1½" sch 40 line from compressed air manifold header
ⓒ
2½" Sch 40
1½" globe va
2½" x 2½" x 1½" reducing lateral
St. wall
2½" nipple Ⓐ
DETAIL D
Conveyor from truck unloader hopper (120 tons/hr)
122'0" c to c pulleys
RECEIVING HOPPER cap - 40.8 tons, 2 hrs 20 ton/hr
Corrugated metal roof
Truck hopper (cap - 5 cu yds)
Unloader (max 120 tons/hr min. 80 tons/hr)
Belt feeder ½ h.p. #
(2.5 tons/hr max variable speed)
Feeder head pulley
COMBUSTION CHAMBER (16.5 million btu/hr max)
Air blower 15 h.p. # 3500 rpm
Air compressor 1½ h.p. # 3500 rpm
Fuel oil pump ½ h.p. # 3500 rpm
DRYER
20 tons/hr
Drive motor 30 h.p. # 1110 rpm
Speed red. (93.51:1)
Fan, 30 h.p. motor # 1760 rpm, 9500 cfm @ 1411 rpm and 33.9 bhp for the fan
Duct to precipitator inlet
DRYER EXHAUST DUST COLLECTOR (cap - 9500 cfm @ 1411 rpm - 33.9 hp)
Trickle va
TE
3 h.p. motor # @ 1800 rpm
BUCKET ELEVATOR (30 tons/hr)
High level indicator and alarm 115 vac - 11 watts
Low level indicator and alarm 115 vac - 11 watts
SURGE TANK 1000 CU FT cap - 48 tons
2.4 hrs @ 20 tons/hr
Manual upper rotary va
C.U. Volumetric ½ h.p. # feeder reeves motor, 30 tons/hr max variable speed
Electric ear
CONTROL PANEL
BALL MILL
20 ton/hr
Gear spray air pump - 4 cfm @ 50 psi nozzles - 5.2 cfm @ 80 psi oper time - 25 to 30 sec. Timer mot and sol valve 120 v. ac
450 h.p. mill drive motor 1170 rpm, 3φ 60 HZ, 4100 volts
For high and low current alarms and indication
EI
10 h.p. motor # @ 190-38 rpm
#108 GYROTOR CLASSIFIER
PI
DUCON DUST CO
cap 25,000 cf
Blast gate
fan and mi
Vent to
10 hp m
Air hea
timer a
compre
@ 100 psi
Rotary a
lock, ½ h.p
TRICKLE VALVE
STORAGE TANK 6600 CU FT. cap - 318.8 tons 15.8 hrs @ 20 ton/hr
NO, NC Limit switch
Air oper rotar
air solenoid va
60 cycle, 110 vol
30 - 100 psi
See DETAIL B
CIRC. FAN, 25,000 cfm @ 1110
125 h.p. # motor, 1760 rpm
8" AT F.W.
10" AT R.W.
3"
8"
6"
4"
F Stub
Durabla ball valve size
Reducer
Min end straight
2½" sch 40
Powell 110 globe valve screwed - size ½"
X
Y
8"
SECTION X-X
½" purge air conn. Ⓣ
20
OUTLET CONN AT DISTRIBUTOR TYP F.W. & R.W.
Plug Ⓣ
Pressure tap
Pressure tap
Orifice Plate
DETAIL A
Service indicator
½" Asco, fig 8210 B-9
Soil filter
120v alarm circuit by TVA
2" safety va
TS
FS
1" oil drain
Drain
Water sight funnel drain
¾" cooling water
FULLER KINYON COMPRESSOR 50 hp motor #
FULLER KINYON
PUMP 30 h.p. m
DETAIL B
As constructed
Added Control Air &
Added Receiver Tank
ATV549-1


Vent
Powerhouse roof
Pressure relief cap vent to atmos
5" feed line
FULLER ALLEVIATOR
20"
Sol. valve assembly with 120v.ac timer (Flex Kleen)
Air header, 7scfm @ 90-100 psi dry air
FLEX KLEEN DUST COLLECTOR
Rotary seal, ½ h.p motor ⊕
½" conn for rotor press. relief (plugged)
Load cell (3) low level alarm and load indication
300 CU FT FEED TANK
cap: 164 tons
43 mins @ 20 tons hr
1½" sampling
SCREW CONVEYOR
3 h.p ⊕ Reeves Motor drive @1800 rpm, with air control sol. valve
½" pressure conn for purging rotor pockets (plugged - typ both seals)
½" conn for rotor press relief (plugged - typ both seals)
5" sch 40
DUST COLLECTOR
000 cfm
gate between
and micro pulsaire
Vent to atmos fan
10 hp motor ⊕
Air header (120v. ac cyclic timer and solenoid valve) compressed air 10.6 scfm @100 psi dry air
MIKRO PULSAIRE
Rotary air-
½ h.p
Seal air to bearings
1" globe valve
Globe valves
4"
Load cell (3) low level alarm and load indication, cut off @ 248 kips each
4" Control valve
Control valves 4"
Safety valve set at 80 psi
Pilot type
4" sch 40
Air receiver tank 6'6" O.D. x 18'-0" long Capacity 550 cu ft
Control Air
Pressure Reducer (75 psi)
From ½" copper supply going up to Flex Kleen and feeders above
6" sch 40
4" Sch 40
4" Ans 1.11
2" safety valve set at 20 psi
½" air, see DETAIL C
Check valve
INJECTION AIR COMPRESSOR 40 h.p motor ⊕ @ 900 rpm
6" sch 40
2" safety va. set at 20 psi
½" air
Check valve
TRANSPORT AIR COMPRESSOR 40 h.p motor ⊕ @ 900 rpm
DISTRIBUTOR (20" O D)
Ball valve, 3" typ
½" purge air conn Ⓣ typ
3½" sch 40 typ
1½" globe valve (typ)
Injection air header El 354'9"
Injection air header El 374'3"
1" globe valves
RW ELEV 364'-6"
RW ELEV 348'-0"
Rear wall
DETAIL-D (TYP)
BOILER
4" sch 40
Front wall
DISTRIBUTOR (16" OD)
FW ELEV 359'-3"
4" globe valve
Globe va., 1½" typ see DETAIL D
Ball valve, 3" typ
½" purge air conn Ⓣ typ
SEE DETAIL "B"
rotary va.
solenoid va.
110 volts
psi
DETAIL B
1½" sampling
@ 1110 rpm and 111.3 bhp
rpm
KINYON TRANSPORT
h.p motor ⊕
LEGEND
GLOBE VALVE
CHECK VALVE
BALL VALVE
HOSE
ORIFICE & PRESSURE TAPS
Ⓣ B&W TERMINAL
S SOLENOID
TS TEMPERATURE SWITCH
FS FLOW SWITCH
GATE VALVE
EI ELECTRICAL INDICATOR
PI PRESSURE INDICATOR
TE TEMPERATURE ELEMENT
PdI PRESSURE DIFFERENTIAL INDICATOR
DIAPHRAGM OPERATED VALVE
PRESSURE REDUCER
5" Air line
½" gate valve
5"x2" red
½" Tryco model B
½" Asco, fig 8210-B-94
5" Moisture separator
2" safety va.
Trap
1" gate valve
5" stream flow check va.
COMPRESSOR
Drain
Air inlet
2"
R.W. line
½" emergency plant air supply (150 scfm) typ both comp
120 v.ac Manzel lube line alert, water sol. valves and high disch air temp. switch by mfr.
DETAIL C
NOTE:
1. ⊕ indicates 3φ, 230/460 v, 60 Hz
Not to Scale

UNIT 10
LIMESTONE INJECTION - SO_2 REMOVAL

SCHEMATIC LOOP
DIAGRAM
LIMESTONE INJECTION

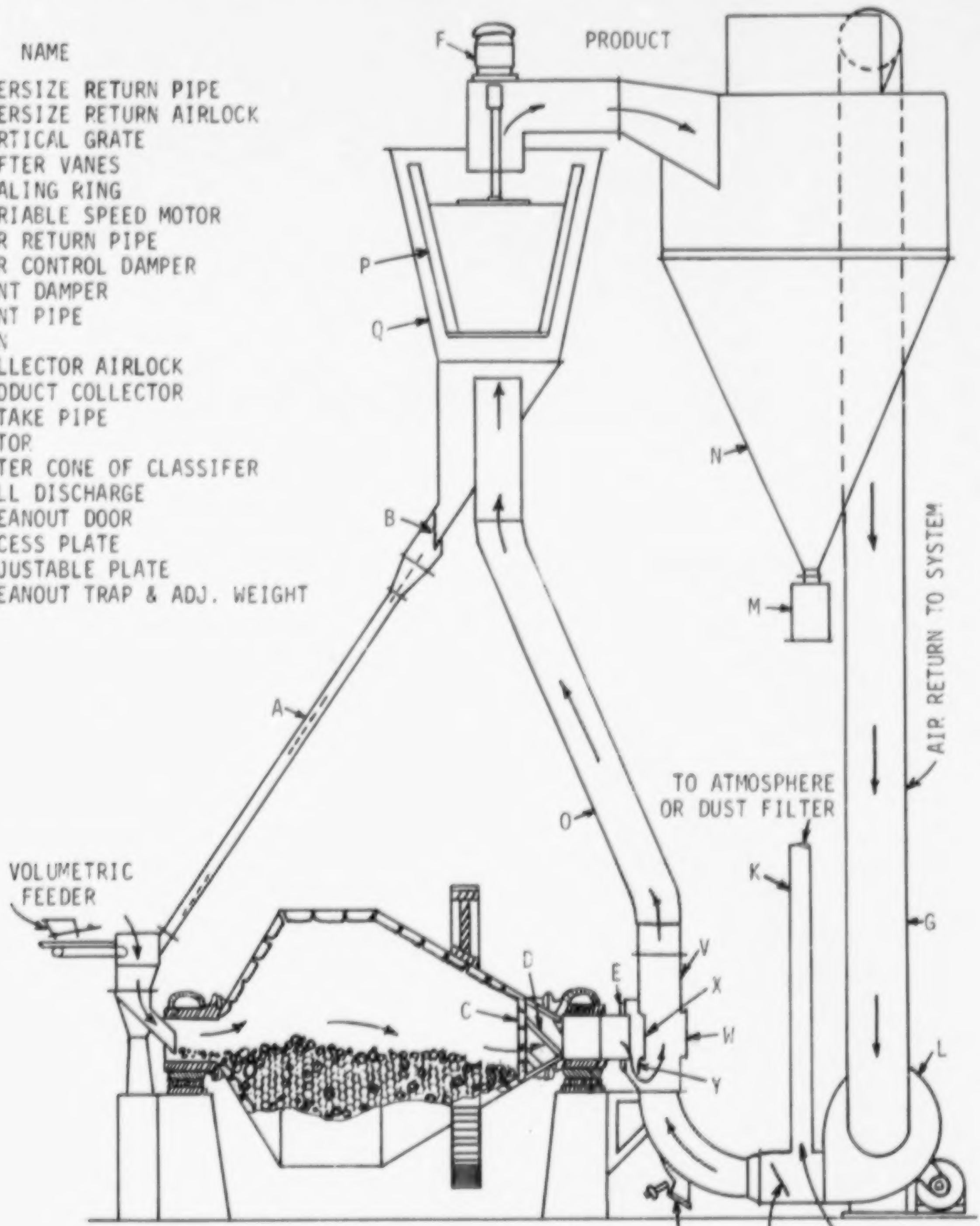
SHAWNEE STEAM PLANT
TENNESSEE VALLEY AUTHORITY
DIVISION OF ENGINEERING DESIGN

SUBMITTED	RECOMMENDED			APPROVED
	Ray H. Graham			J.P. Parrish
KNOXVILLE	3-17-69	35	M	4 47W549-1 R3

FIGURE 7

GENERAL ARRANGEMENT OF HARDINGE MILL AND GYROTOR CLASSIFER WITH TRUNNION OVERFLOW TYPE DISCHARGE

KEY	NAME
A	OVERSIZE RETURN PIPE
B	OVERSIZE RETURN AIRLOCK
C	VERTICAL GRATE
D	LIFTER VANES
E	SEALING RING
F	VARIABLE SPEED MOTOR
G	AIR RETURN PIPE
H	AIR CONTROL DAMPER
J	VENT DAMPER
K	VENT PIPE
L	FAN
M	COLLECTOR AIRLOCK
N	PRODUCT COLLECTOR
O	UPTAKE PIPE
P	ROTOR
Q	OUTER CONE OF CLASSIFER
V	MILL DISCHARGE
W	CLEANOUT DOOR
X	ACCESS PLATE
Y	ADJUSTABLE PLATE
Z	CLEANOUT TRAP & ADJ. WEIGHT


F
PRODUCT
P
Q
N
B
M
A
AIR RETURN TO SYSTEM
TO ATMOSPHERE OR DUST FILTER
O
K
G
VOLUMETRIC FEEDER
D
E
V
X
C
W
L
Y
Z
H
J

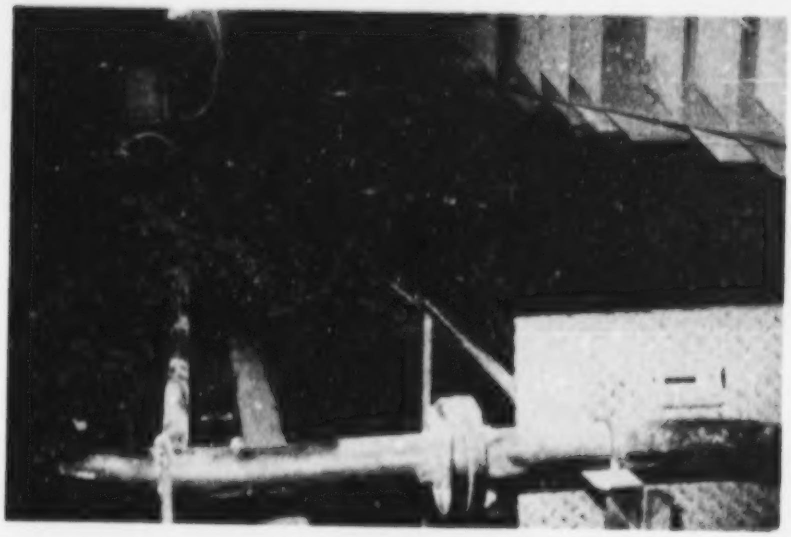


Figure 8
Limestone Distributor Can
Located at Rear of Boiler

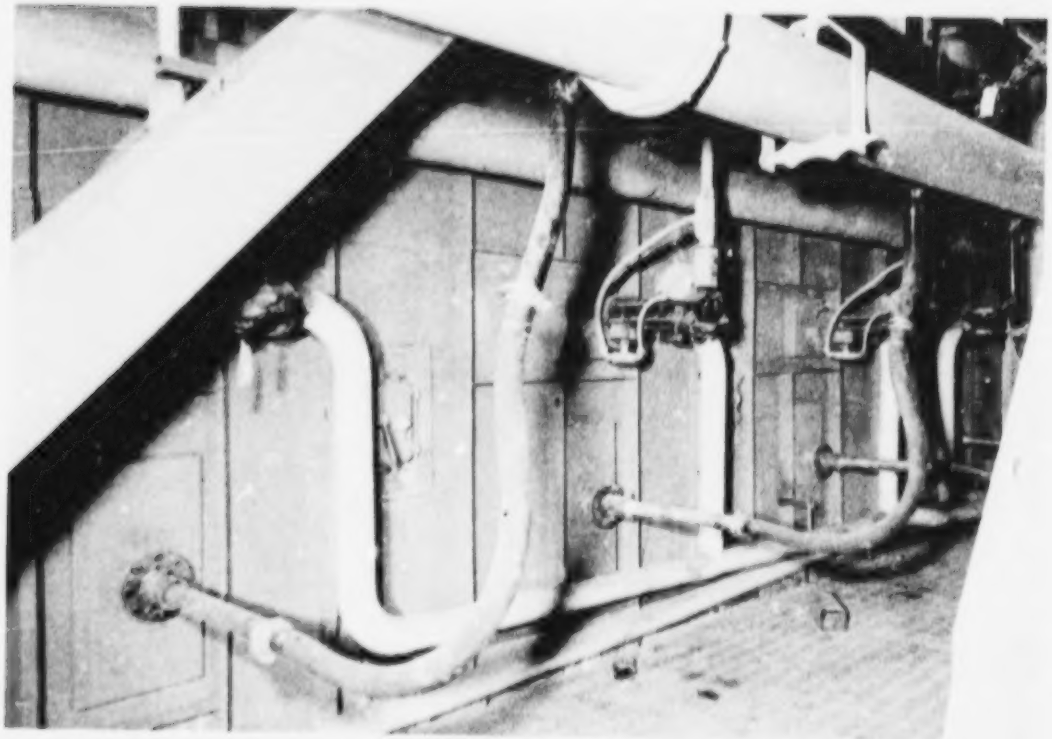
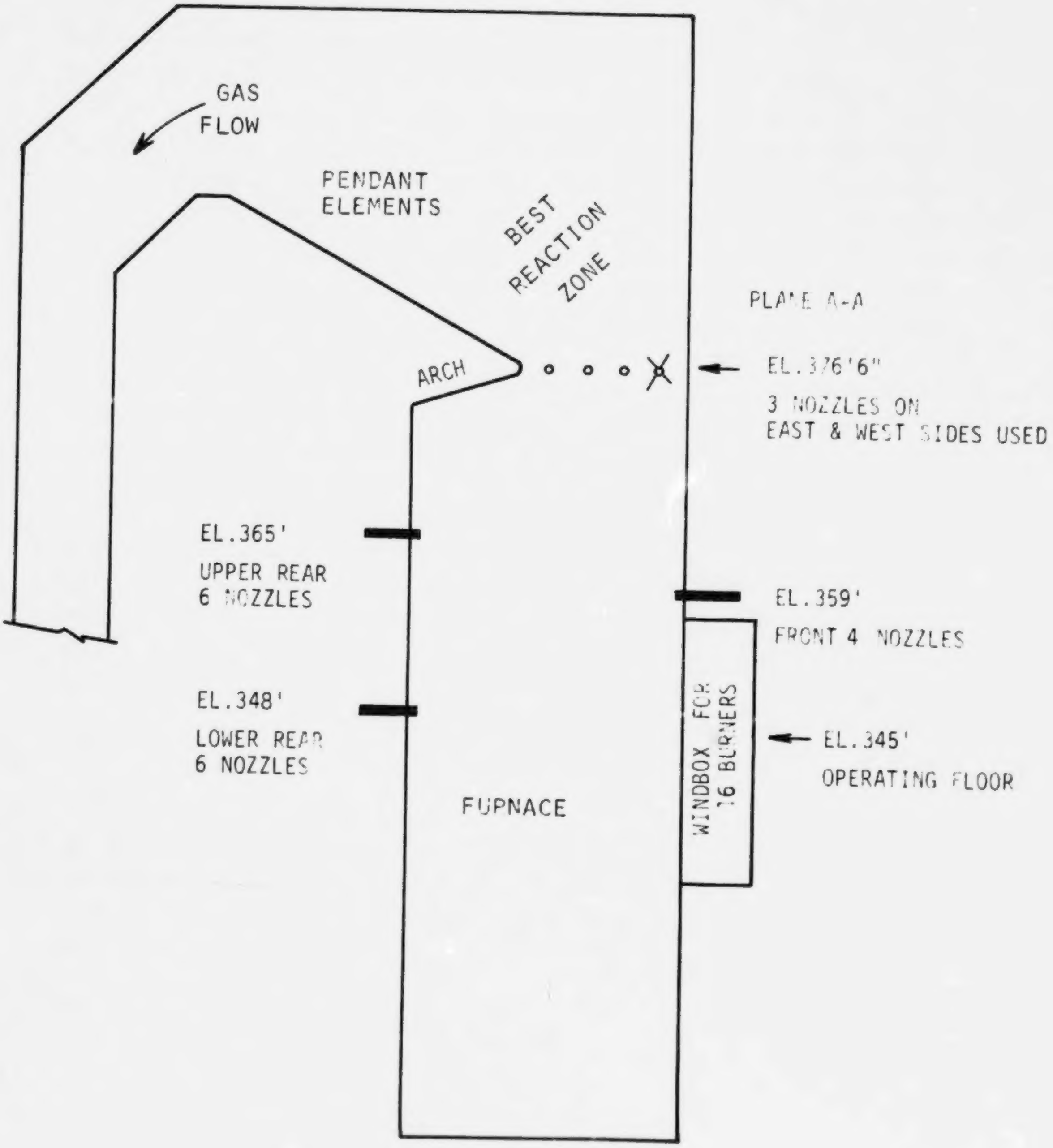


Figure 9
Limestone Injection System (SO_2 Removal)
Limestone Injection Nozzles at Rear of Unit 10 Boiler
El. 345

FIGURE 10

SHAWNEE UNIT 10

LIMESTONE INJECTION SITES


GAS FLOW
PENDANT ELEMENTS
BEST REACTION ZONE
PLANE A-A
ARCH
EL.376'6"
3 NOZZLES ON EAST & WEST SIDES USED
EL.365'
UPPER REAR 6 NOZZLES
EL.359'
FRONT 4 NOZZLES
EL.348'
LOWER REAR 6 NOZZLES
WINDBOX FOR 16 BURNERS
EL.345'
OPERATING FLOOR
FURNACE

3. Sampling Stations

Process testing involved sampling inputs and outputs at those locations postulated to yield representative samples. Solids, liquid, and gas sampling was carried out during the program with most locations as shown in Figure 11. Perhaps the most important and certainly the most technically difficult sampling was at the furnace outlet, designated the A-A plane. The dust distribution study (Phase II of the test program) required sampling across this plane yet no probes existed to accomplish this task. Therefore, concurrent with the design phase of the program a development project on water-cooled probes was undertaken by TVA. A water-cooled probe was designed, fabricated and tested which was capable of taking average isokinetic dust samples from furnace gas. The probe measured gas temperatures and velocity pressures as required for determination of average isokinetic sampling parameters at any given sampling point. To accomplish the extensive sampling there were four of the moveable probes on each side of the furnace at the A-A plane and three at the B-B plane. Figure 12 shows these probes while more detail regarding their construction and development is given in appendix B. The frequency and location of sampling varied with test requirements.

4. Laboratory Capability

An on-site laboratory housed in a trailer was required for daily analyses for coal sulfur content, particle size measurement, limestone moisture content, hydration study and chemical analysis on limestone modified fly ash dust samples. Some samples were analyzed on-site while others were given more complete study at the TVA Central Laboratory in Chattanooga. Coal samples obtained from feeder scales were prepared in a special enclosure in the powerhouse before analysis in the field laboratory. The water Quality Branch also performed on-site analyses of sluice water obtained prior to and during the test program. This facility met project requirements. Minor problems concerned providing adequate air conditioning and stabilizing support for analytical balances within the trailer.

FIGURE 11

SHAWNEE UNIT 10 SAMPLING STATIONS

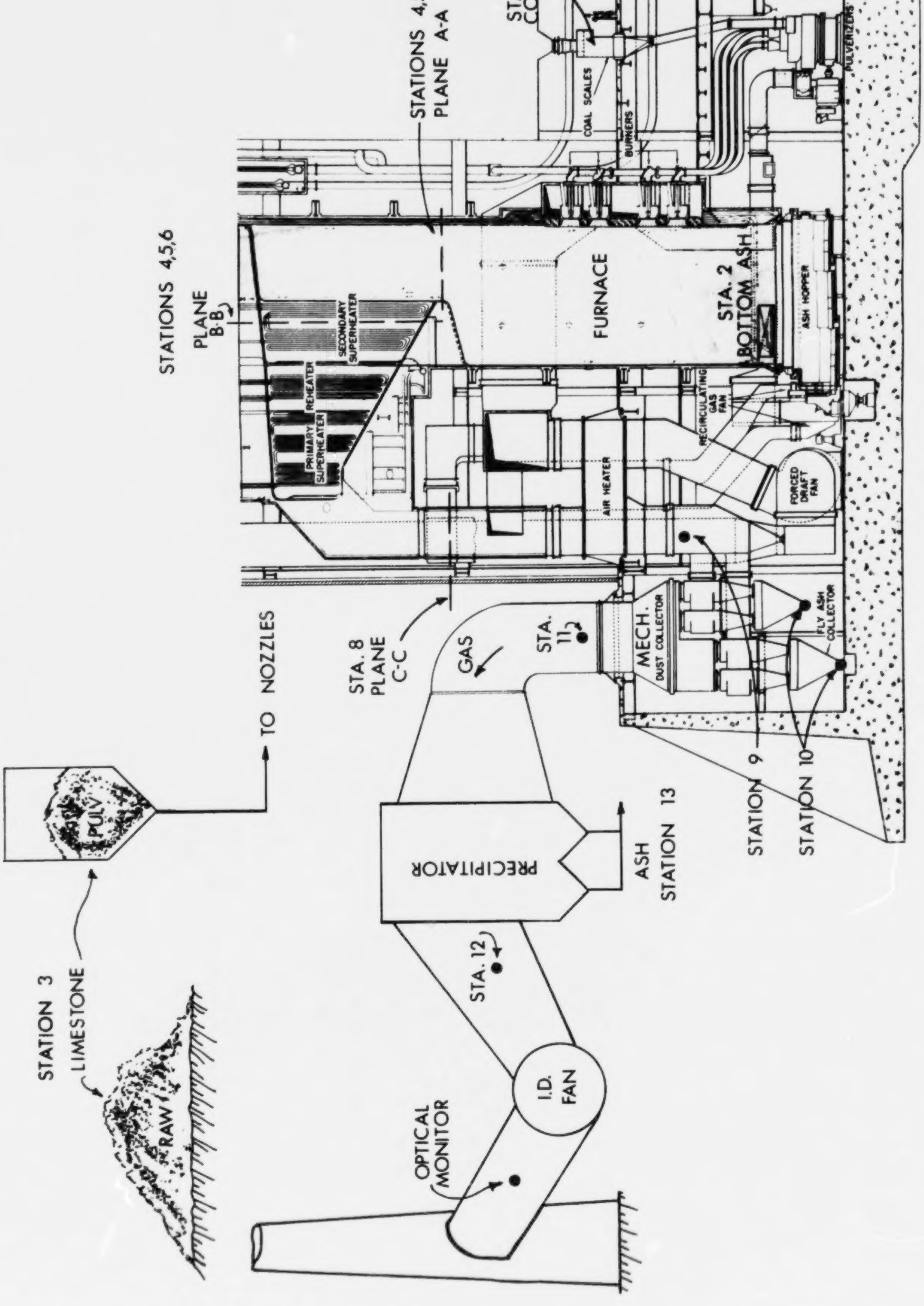
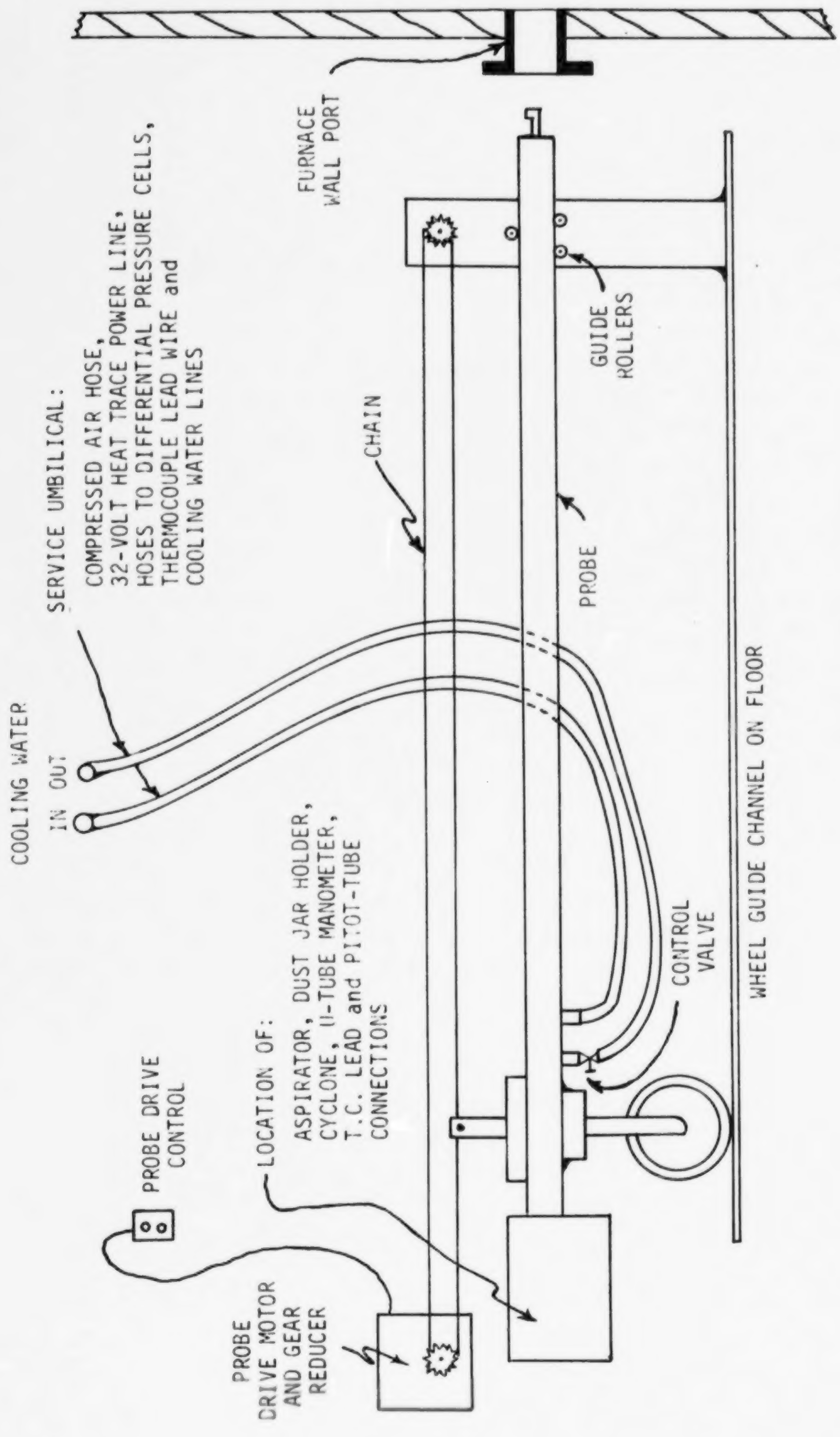

STATION 3
LIMESTONE
RAW
PULV
TO NOZZLES
OPTICAL MONITOR
I.D. FAN
STA. 12
PRECIPITATOR
ASH STATION 13
GAS
STA. 8 PLANE C-C
STA. 11
MECH. DUST COLLECTOR
FLY ASH COLLECTOR
STATION 9
STATION 10
AIR HEATER
FORCED DRAFT FAN
RECIRCULATING GAS FAN
PRIMARY SUPERHEATER
REHEATER
SECONDARY SUPERHEATER
STATIONS 4,5,6 PLANE B-B
FURNACE
STA. 2 BOTTOM ASH
ASH HOPPER
STATIONS 4,5,6,7 PLANE A-A
BURNERS
COAL SCALES
STA. 1 COAL
PULVERIZERS

FIGURE 12

GENERAL ARRANGEMENT OF WATER-COOLED PROBE


FURNACE WALL PORT
GUIDE ROLLERS
CHAIN
PROBE
SERVICE UMBILICAL:
COMPRESSED AIR HOSE, 32-VOLT HEAT TRACE POWER LINE, HOSES TO DIFFERENTIAL PRESSURE CELLS, THERMOCOUPLE LEAD WIRE and COOLING WATER LINES
COOLING WATER
IN OUT
WHEEL GUIDE CHANNEL ON FLOOR
CONTROL VALVE
LOCATION OF:
ASPIRATOR, DUST JAR HOLDER, CYCLONE, U-TUBE MANOMETER, T.C. LEAD and PITOT-TUBE CONNECTIONS
PROBE DRIVE CONTROL
PROBE DRIVE MOTOR AND GEAR REDUCER

C. PHASE I SHAKEDOWN

1. OBJECTIVES

System Startup and Initial Operation best describe Phase I. Objectives of these preliminary tests and calibrations were:

a. Determine operating characteristics of limestone handling, grinding, and injection system.

b. Establish reliable sampling and measurement techniques, analytical and calculational procedures for rapid determinations.

c. Check the performance and accuracy of equipment under actual test conditions.

d. Observe boiler operating and performance characteristics during limestone injection.

e. Establish the operating range of variables to be investigated in the test program.

f. Determine the nature of temperature, velocity, SO_2 and dust distribution in the boiler furnace.

2. APPROACH

As equipment was turned over from Construction for initial operation, tests were begun to accomplish the above objectives. These included calibration of load cells under the storage and feed tanks; calibration of the gyrotor classifier to obtain correlation of speed versus limestone particle size; determine the operability of the water-cooled probes and make improvements where necessary; check out all procedures set up for sample collection at coal scales and ash sampling locations; determine the possibilities of making mass balances by analysis of bottom ash samples; obtain preliminary data on temperature, velocity, O_2, SO_2 and CaO concentration of flue gas at the furnace outlet (A-A) and boiler outlet (C-C) planes; determine the operability and accuracy of laboratory techniques. There was need to train the test observers who operated the probes, obtained material samples and took test data.

Some of the key process variables and their design influence in the test program required evaluation during Phase I and are discussed next.

a. Injection Velocity and Angle

The required injection velocity for good distribution was not predictable with a high degree of confidence so the system was designed to provide a variable nozzle velocity ranging from 60 to 130 feet per second. A steam injection system was added to increase velocity if it appeared air alone were inadequate to obtain jet penetration. The four front nozzles injected only at the horizontal or 0° because of structural limitations. Upper and lower rear nozzles were of two types: straight nozzles for horizontal or 0° injection and bent nozzles (rotatable) for 45° upward or 45° downward injection. The theory was that some change in particle residence time would result from jets entering at various angles.

For the optimization tests (Phase III of the test program) nozzles were shaped to provide ± 25° and 0°. Later, in Phase IV, nozzles of -25° were used at the A-A plane. All were constructed of type 316 stainless steel.

b. Injection Temperature

The temperature environment of the injected limestone particles will be influenced mainly by the point of injection. For design purposes it was assumed that nozzles should be installed at boiler elevations corresponding to desired gas temperatures. Based on the results of full-scale injection tests in Germany[3] and in this country it was concluded that injection should be where minimum gas temperature is about 2400 °F and maximum of 2900 °F. This range was expected to provide flexibility for evaluation of temperature effect on a given stone and for selecting alternate temperatures for various stones. Small scale studies[4] showed particle heat up to be accomplished in a few hundredths of a second and is shown schematically in figure 13. In consideration of these temperature limitations and nozzle installation possibilities the injection locations were designed.

c. Limestone Type

Selection of limestone for a specific application of the process will be based on cost which in turn is influenced by delivered price, reactivity, and grindability. Potential suppliers within a 200-mile radius of the plant were asked to provide quotations and samples of materials they could supply in the quantities required. These samples were analyzed for chemical and mineral components, tested for grindability, and subjected to small-scale and pilot plant tests for reactivity. Based on results of these tests, stone was selected for the main portion of the test program that had the best potential for low operating cost and high sulfur dioxide removal potential.

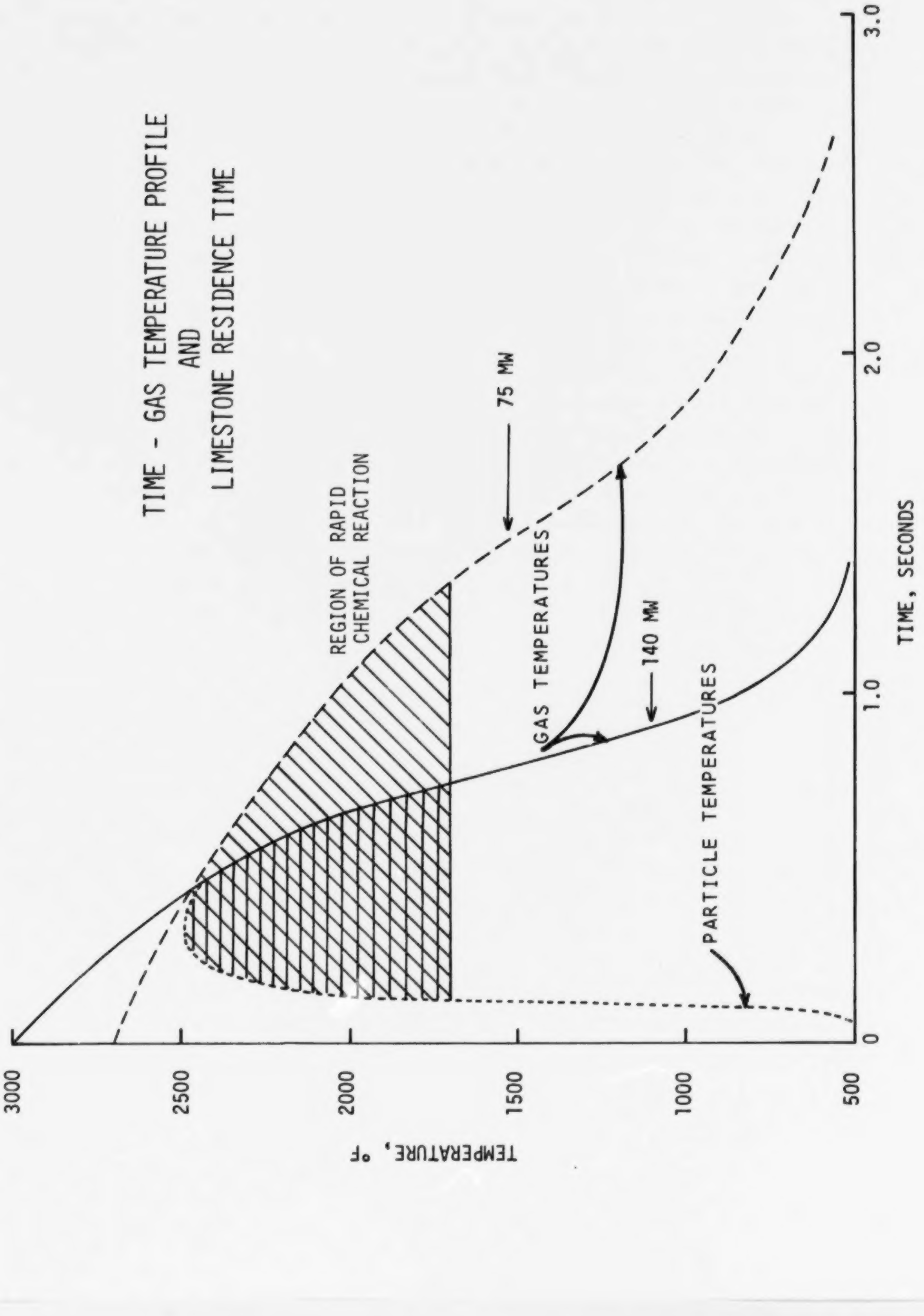
d. Stoichiometry

Based on a conceptual design and economic study[2], addition of more than 200 percent of the stoichiometric amount of limestone for the assumed sulfur level was not expected to be practical because of cost and operational limitations (temperature control, erosion, dust collection, waste disposal). However, it was desirable to evaluate effects of stoichiometry on the process and boiler operations. For this reason, facilities were provided to inject from 50 percent to 400 percent stoichiometric at 150 MW load. Another factor affecting stoichiometry is coal sulfur content. The coal supply for the Shawnee plant is purchased on several contracts and when possible the receipts from various mines are unloaded directly to the bunkers to prevent reclaiming from stockpile. Therefore, the supply during test periods was sometimes subject to variations ranging as widely as composition of receipts. Sulfur content ranging from about 1.0% to 5.5% and ash contents from 9 to 25 percent have been reported. An average sulfur level of 2.7% was assumed for design purposes. To some extent during the test program, sulfur level was controlled by segregating selected shipments.

e. Limestone Particle Size

The importance of particle size was not clearly defined at the time of system design. An increase in degree of limestone utilization might be offset by loss of reactivity due to overheating as particle size is reduced beyond a certain point. For design purposes it was assumed that maximum fineness should be 70% - 325 mesh (44 μ).

FIGURE 13



TIME - GAS TEMPERATURE PROFILE
AND
LIMESTONE RESIDENCE TIME

f. Moisture

Although most stones are dense and have low absorbed moisture the surface moisture varies widely making a pre-dryer for the mill feed essential. Pulverization to micron size is more efficient if stone moisture is less than 1%.

3. RESULTS

a. Limestone Weighing and Feeding

The weighing system was remarkably stable with only minor corrections required over most of the load range. Calibration curves for limestone feed and storage tanks are shown in figures 14 and 15. Weight measurements from the feed tank are accurate to within ± 1% over most of the operating range. Actual weights of limestone injected were based on difference readings over time intervals, often at three minutes, to assure average rate linearity.

b. Limestone Grinding

Capacity of the ball mill depends on feed size and the reject rate from the gyrotor classifier. Feed was minus 1-1/2" with considerable fines included. Pulverized stone leaves the mill and enters the classifier which at slowest speed (20% or 38 rpm) provided 20 tons per hour product size. At highest classifier speed (100% or 190 rpm) the mill capacity dropped to about 6 TPH. For grindability not less than 50 Hardgrove the expected mill performance was as follows:

% - 325 Mesh	Net Tons Per Hour
70	20
75	18
80	16
85	14
90	12
95	9

c. Particle Size Classification and Measurement

Early in the program comparisons were made on several instruments for particle size measurement. The Bahco instrument was found suitable for size distribution whereas the Fisher Sub-Sieve Sizer was best for field laboratory service where mean particle index served operating needs. The procedure for the Fisher instrument is simple, fast, and gives repeatable results. See appendix C for more details.

The gyrotor classifier speed was found to yield a rather limited particle size range with Fredonia limestone. This is shown in figure 16 were a curve for aragonite limestone (used in Phase III) is also included. Typical results on Fredonia limestone are as follows:

CALIBRATION CURVE FOR LIMESTONE FEED TANK

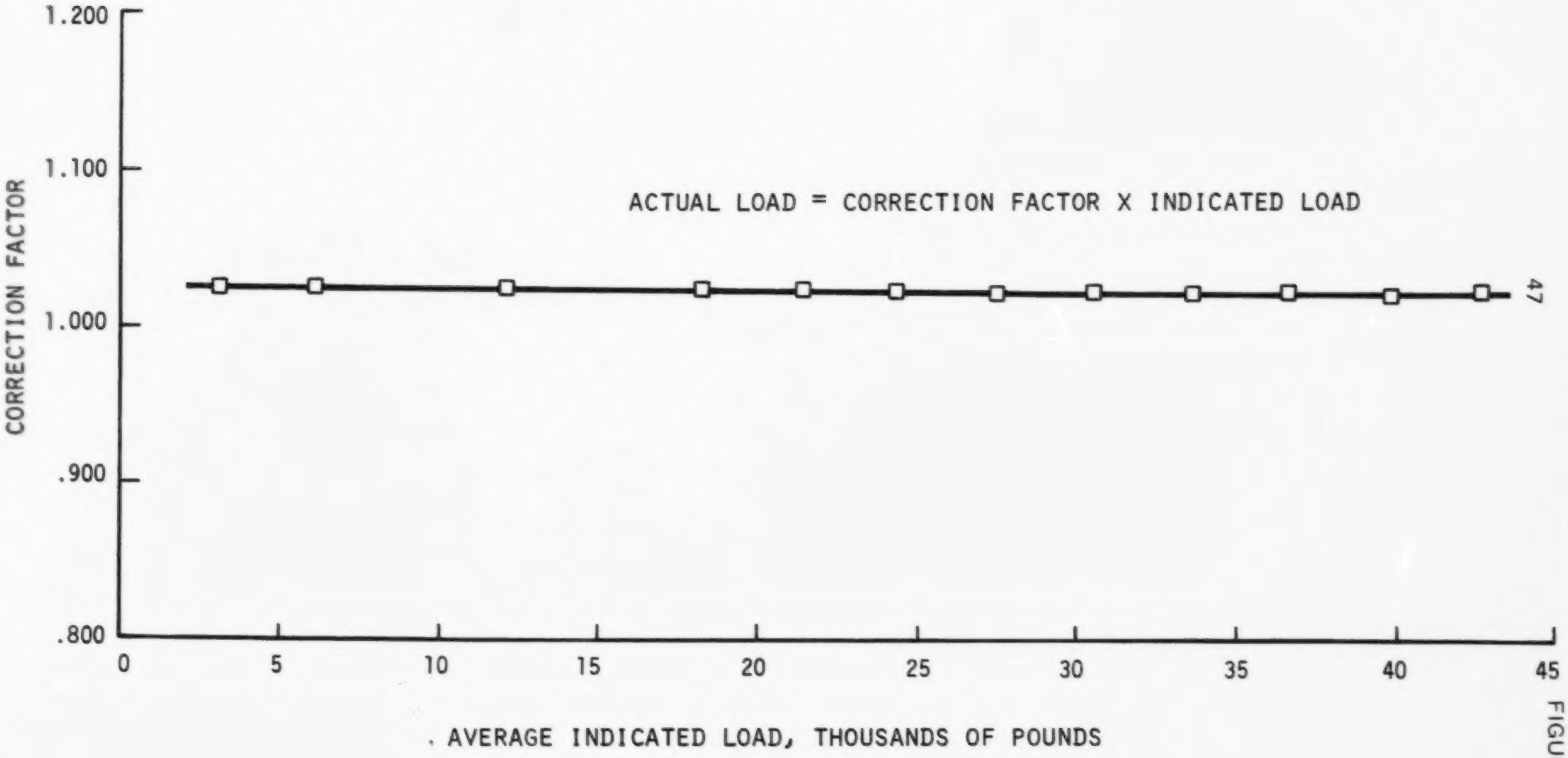
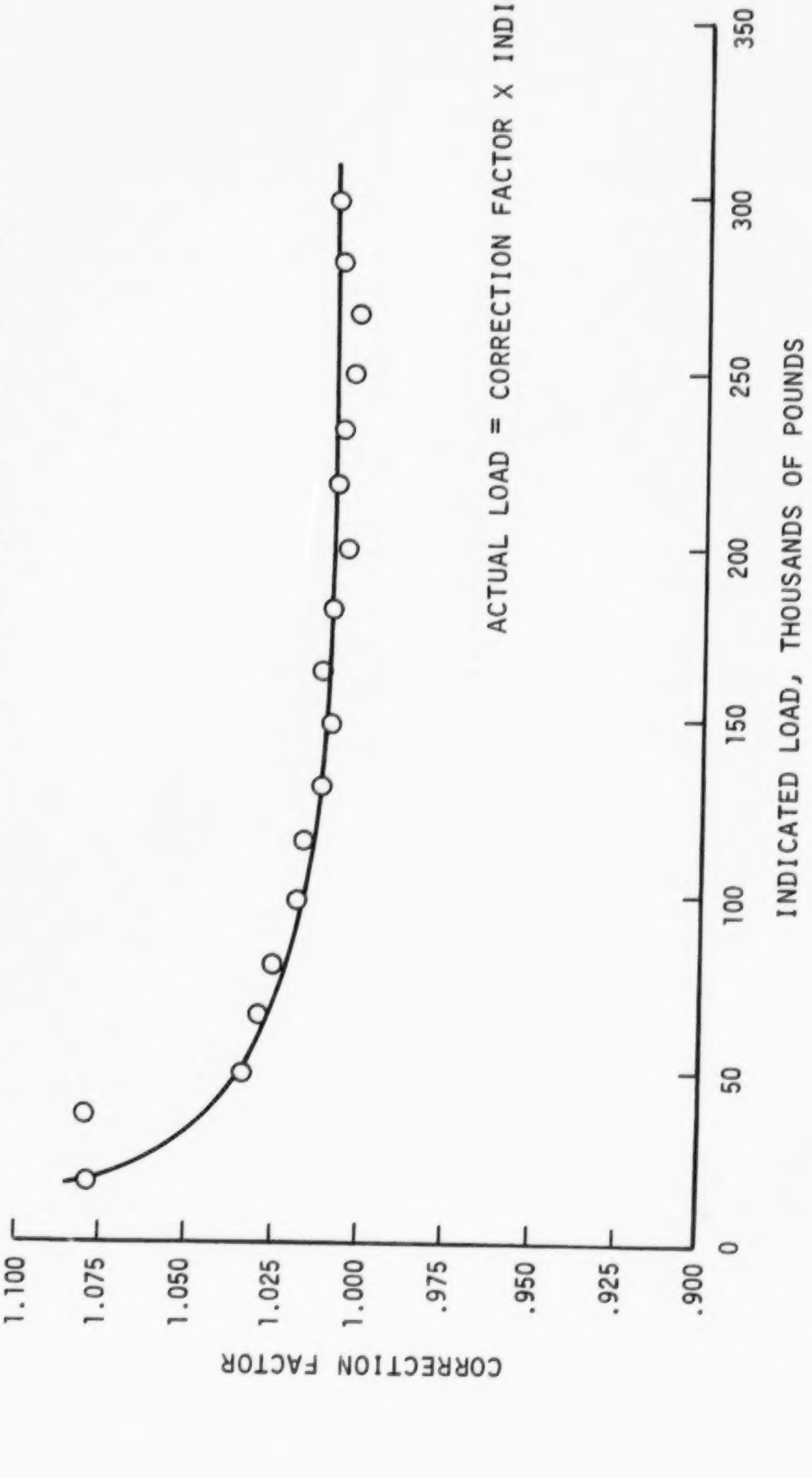


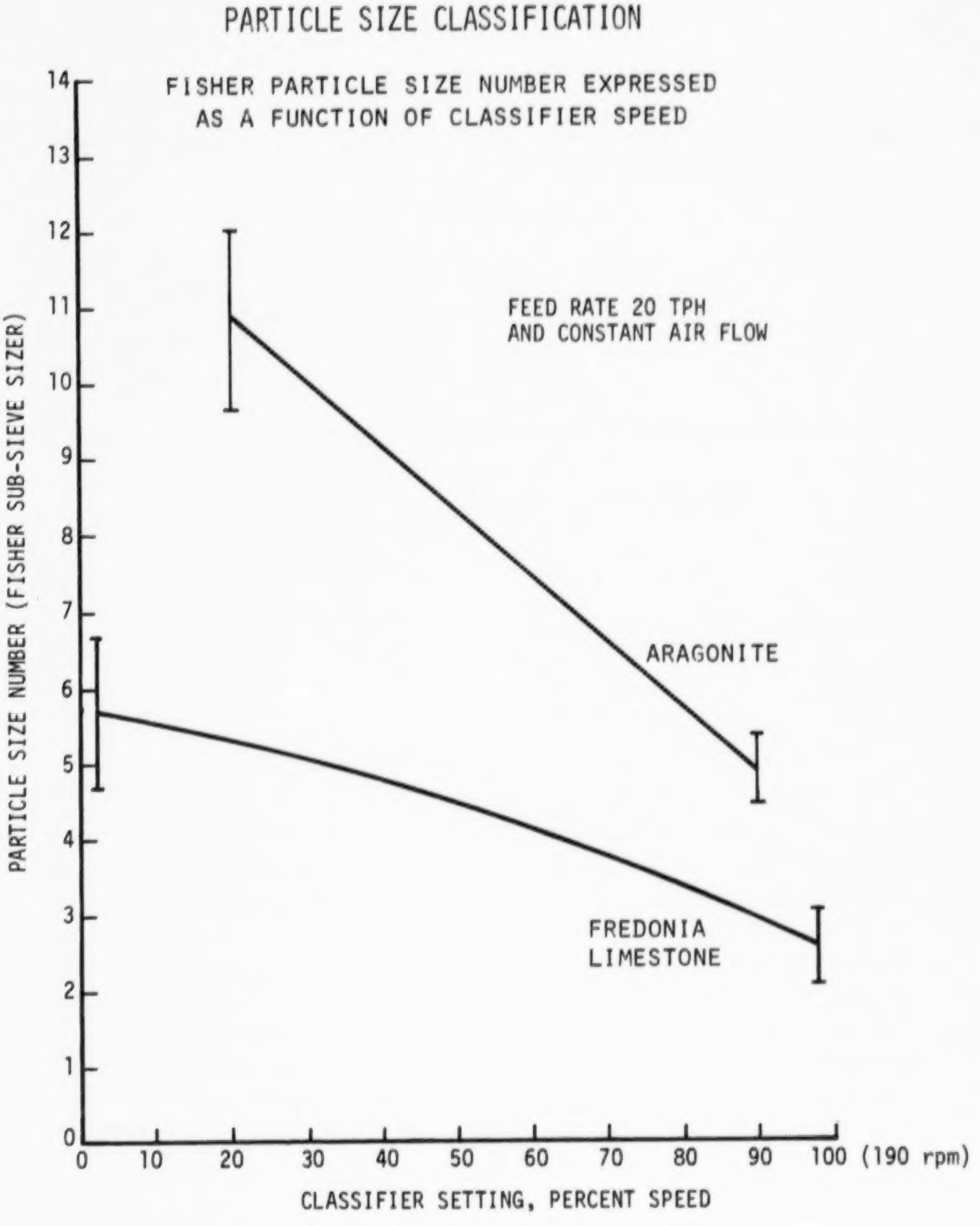
FIGURE 14

CALIBRATION CURVE FOR LIMESTONE STORAGE TANK



ACTUAL LOAD = CORRECTION FACTOR X INDICATED LOAD

FIGURE 16


PARTICLE SIZE CLASSIFICATION
FISHER PARTICLE SIZE NUMBER EXPRESSED AS A FUNCTION OF CLASSIFIER SPEED
FEED RATE 20 TPH AND CONSTANT AIR FLOW
ARAGONITE
FREDONIA LIMESTONE
PARTICLE SIZE NUMBER (FISHER SUB-SIEVE SIZER)
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
0
10
20
30
40
50
60
70
80
90
100 (190 rpm)
CLASSIFIER SETTING, PERCENT SPEED

Sample No.	Classifier Setting %	Percentage Retained on U.S. Standard Sieves					Passing
	%	60	100	200	325	400	-400
432	20	5.8	25.7	0.2	7.2	2.7	58.3
454	80	0.1	5.6	0.4	4.7	2.5	86.8

Other physical characteristics determined for numerous samples during this period, typical results are as follows:

Sample No.	Density g/ml	Blaine Fineness cm^2/g	Mean Particle Dia. Microns	Surface Area cm^2/cm^3
432	2.79	4930	4.4	13740
454	2.65	6250	3.6	16570

The size distribution was determined on Bahco equipment and yielded these typical values:

Sample 432*

% less than	μ size
28.8	5.7
39.0	8.6
43.4	11.8
47.5	16.0
53.2	21.4
56.2	26.2
57.2	29.0

*Sample 454 was too fine to run on Bahco equipment.

d. Limestone Injection Velocity

Control over this important variable was by use of one or two air compressors and the supplemental steam. In the original design, one compressor supplied sufficient air to provide nozzle exit velocity of 60 feet per second as limestone transport air while use of the second compressor increased this velocity to 130 feet per second by its introduction to the transport line just ahead of the nozzles. Supplemental steam was available at 125 psig and combined with the total air flow at the nozzle discharge. Calculated injection velocity benefits were based on momentum exchange. It appeared to improve SO_2 removal to a small extent when introduced shortly after having begun limestone injection. On other occasions its benefit was not detected. Limited observation of jet penetration was possible through inspection doors in the furnace. The limestone jet generally lost identity about 6 to 8 feet from the nozzles.

Installation of an air receiver later in the program provided pressure of about 12 psig for injection but static pressure at the nozzle was down to about 1 psig.

e. Injection Site Temperature

The gas temperature prevailing at limestone injection sites was of particular interest. Therefore, traverses were conducted at locations where long probes could be inserted. Injected limestone particles are heated by radiation and convective heat transfer both of which also influence temperature measuring techniques.

The development of water-cooled probes became necessary to determine gas temperatures, and velocity pressures so that dust samples could be obtained by isokinetic gas sampling at each point in the traverse. Details of probe development and operating procedures are given in appendix B. Gas temperatures were obtained by the use of shielded high velocity thermocouples, operated in accordance with established procedures.

Temperature profiles were determined in the plane of the lower rear injection site and at the furnace outlet (Plane A-A). The profiles are steep both vertically and horizontally in the furnace as shown in figure 17. In this case the temperature change from the wall to the center of the furnace plane approximates the change in temperature vertically between these two planes, lower rear versus plane A-A. Cross-sectional area of the plane A-A is a little more than half the lower furnace area and, therefore, contributes to a steeper gradient. Note that the temperature at the lower rear near the wall appears acceptable for limestone injection but exceeds the desired value within the zone of greater combustion activity. Temperature at the A-A plane appears well within design injection temperatures. Figure 18 shows a typical horizontal temperature profile of gas leaving the furnace through the west half of plane A-A. (Similar 24-point traverses were obtained on the east half). The temperature spread is from 1600 °F to 2500 °F with the lower temperatures appearing in corners and at isolated points near the furnace wall. Hottest gas generally pass this section on the rearward side of the centerline, as shown in this isothermal plot. Gas velocities measured at these same points are plotted in figure 19, and generally range from 20 to 75 feet per second. Typical minimum and maximum velocity profiles appear in figures 20 and 21, respectively. There was no evidence of significant temperature pulsation at constant load yet an average velocity pulsation of about 20 feet per second had been measured. The significance of this pulsation on the SO_2 removal process is unknown.

FIGURE 17

TYPICAL TEMPERATURE PROFILES IN FURNACE

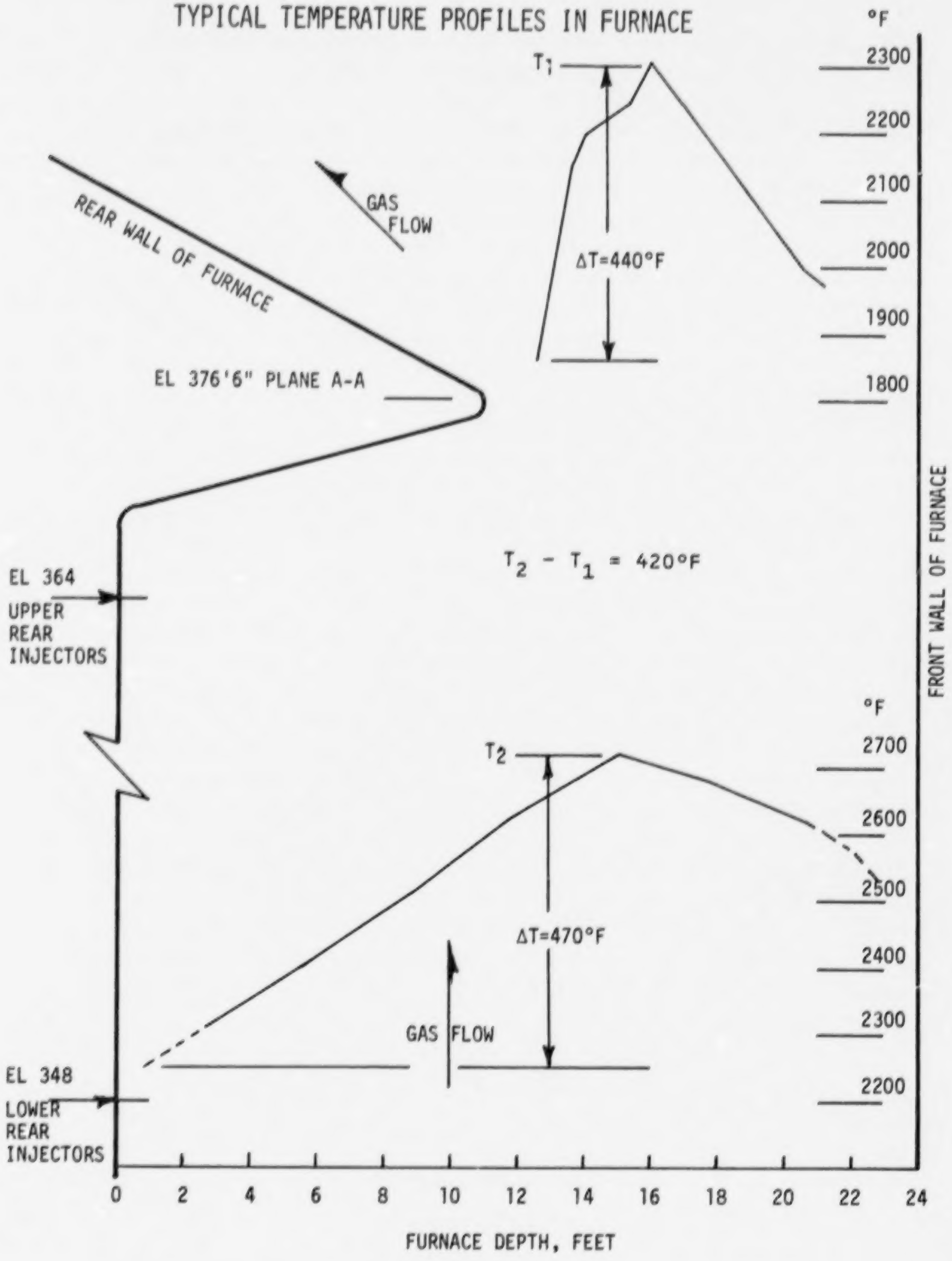
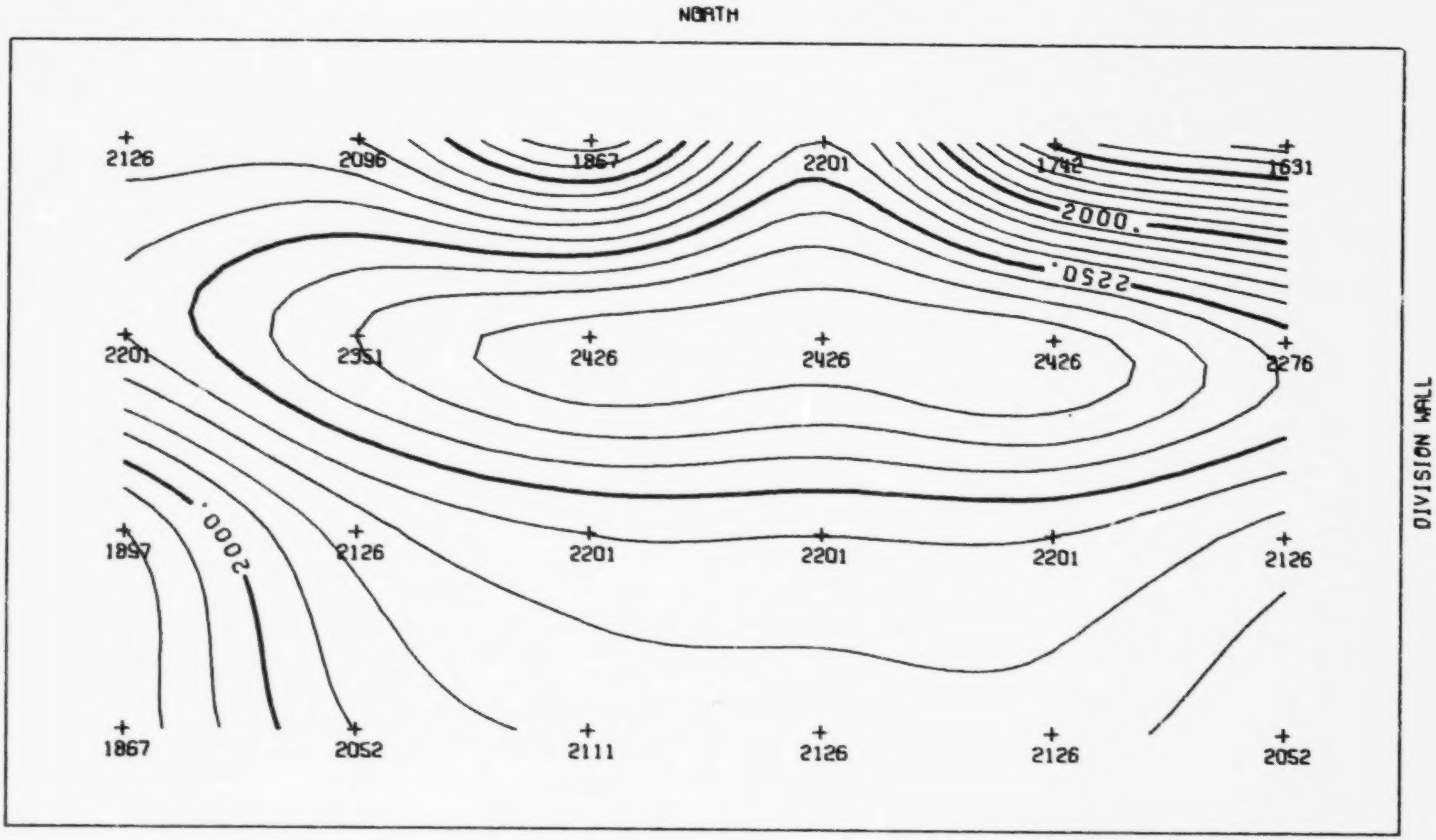


FIGURE 18



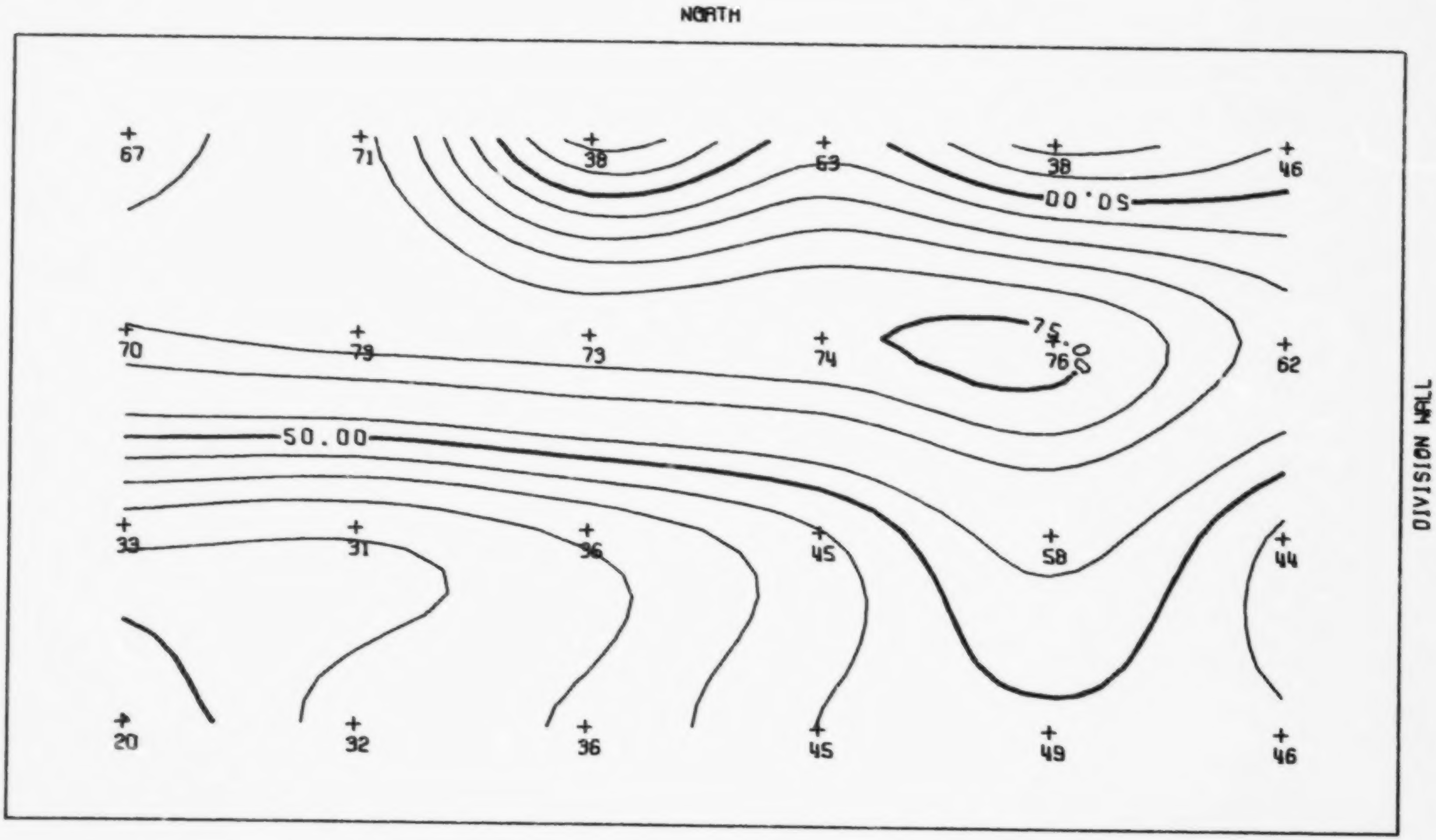
PLANE A-A WEST 5-12-70 TEST 1

ISOTHERMS - INTERVAL = 50 DEG F

Test Conditions

Unit load 140 MW, excess air 24%
Plane A-A avg. temp. 2127 °F
Injection at lower rear @ 0°
Fredonia limestone @ 1.68 stoich.

FIGURE 19

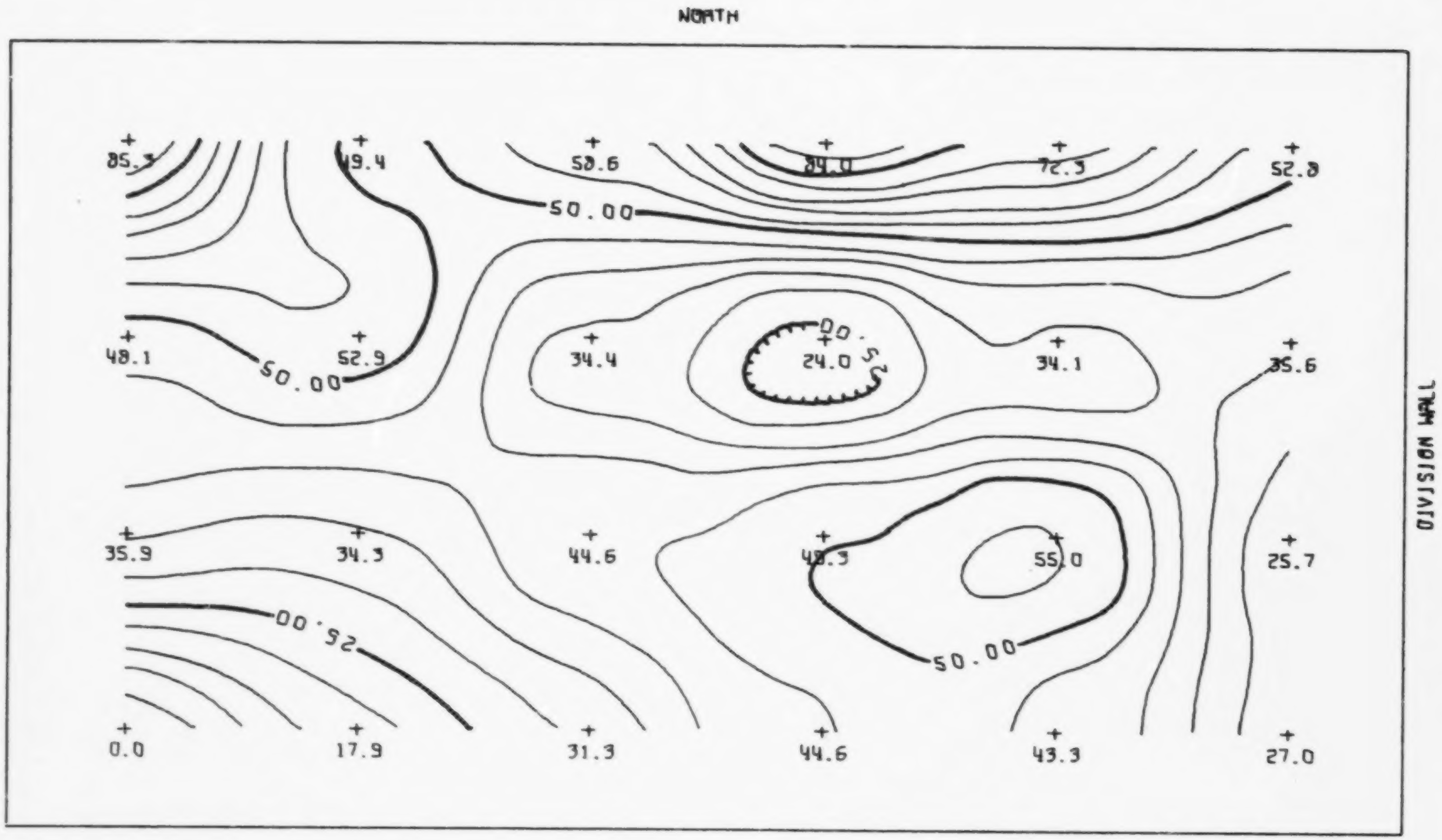


PLANE A-A WEST 5-12-70 TEST 1

ISOVELS - INTERVAL = 5 FT/SEC

Test Conditions

Unit load 140 MW
Plane A-A avg. velocity 51 fps
Injection at lower rear
Fredonia limestone



PLANE A-A WEST 01-14-71 TEST S101

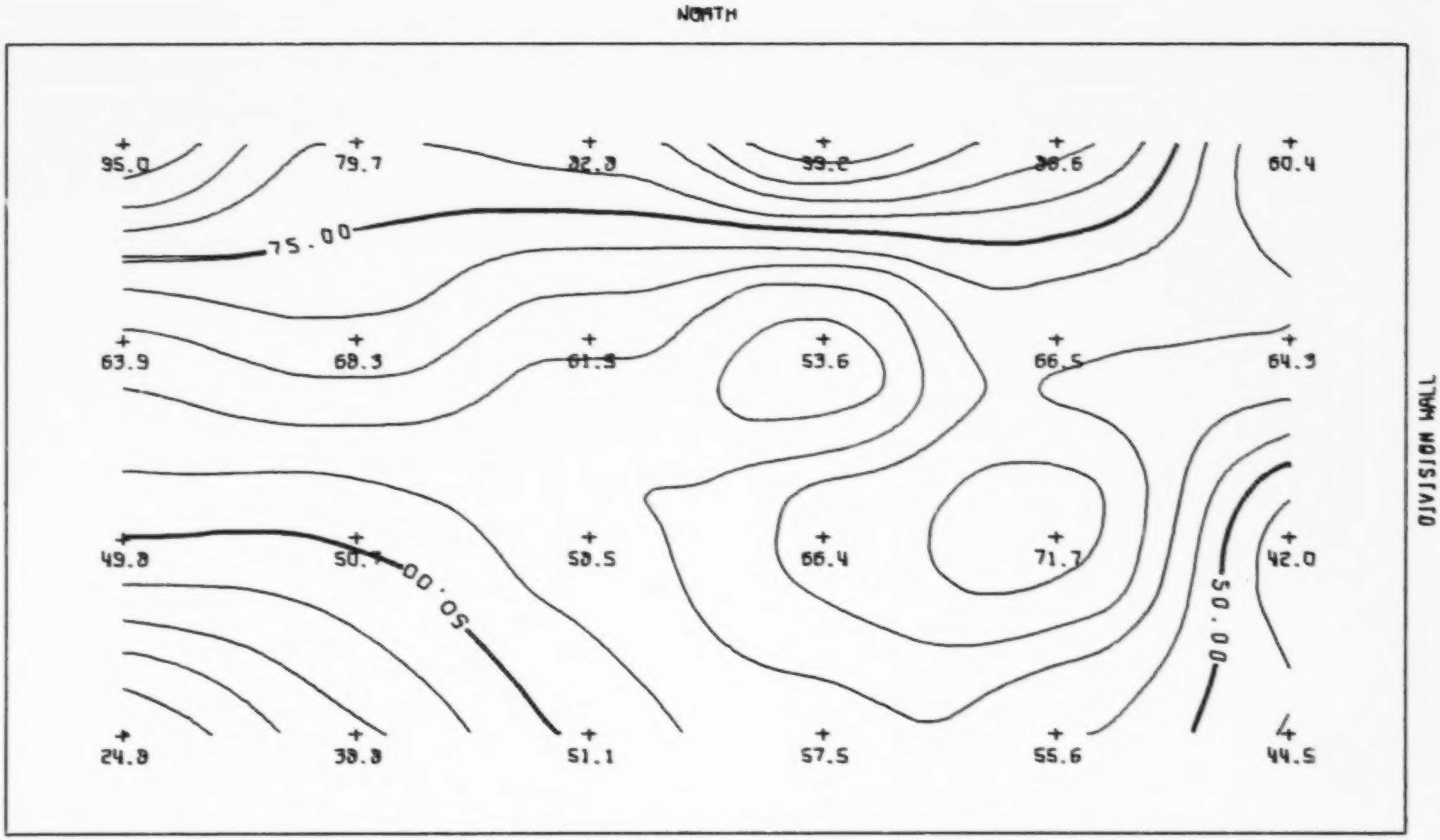
ISOVELS - INTERVAL = 5 FT/SEC

Test Conditions

Unit load 140 MW, excess air 30%
Plane A-A avg. velocity 45 fps

FIGURE 20

FIGURE 21



PLANE A-A WEST 01-14-71 TEST S102

ISOVELS - INTERVAL = 5 FT/SEC

Test Conditions

Unit load 140 MW, excess air 30%
Plane A-A avg. velocity 63 fps

f. Sampling and Measurements

In order to adequately monitor the process several sampling stations were located throughout the boiler cycle, as shown in figure 11. A description of each point is as follows but actual sampling procedures are covered in appendix C.

Station 1. Coal samples were withdrawn from four coal scales just before the pulverizers, each of which supplies a row of four burners. The combined coal sample was prepared for laboratory analysis by standard preparation methods.

Station 2. Ash that falls into the furnace bottom was sampled to determine if it contained significant quantities of limestone fallout. After analyzing sufficient samples it was determined that this test point would be seldom used.

Station 3. Limestone samples were taken from the feed tank by a long thief pipe dropped into a tankfull. Openings at numerous points along this thief pipe provided representative samples for a composite. This test station also covers incoming raw limestone.

Stations 4-7 located on each side of the boiler at plane A-A provided access for water-cooled probes by which temperature and velocity pressure were measured prior to obtaining isokinetic dust samples. Occasionally, SO_2 and 0_2 measurements were taken via these probes. Points 4, 5, and 6 were repeated in the plane B-B.

Station 8. This is the plane C-C or boiler outlet and the location where the sulfation reaction is essentially complete. A fixed network of gas sampling points was located here with continuous SO_2 monitoring by two ultraviolet analyzers. Average SO_2 levels for the east and west furnaces were recorded on strip charts for this sampling station. Furance gas flow divides again at this elevation before entering regenerative air preheaters.

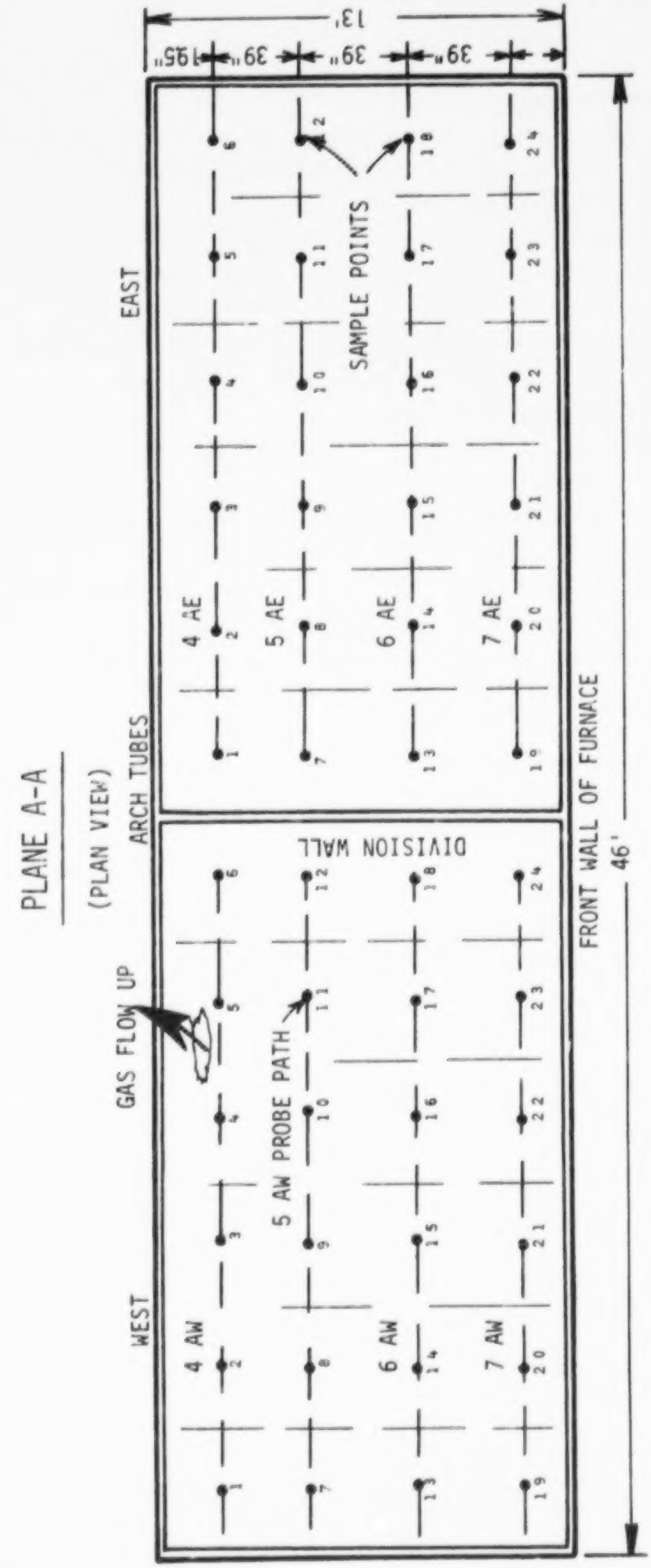
Station 9-13. Fly ash was sampled through these locations. Stations 10 and 13 were at the main sluice pipes from mechanical collectors and precipitator hoppers, respectively. Stations 9, 11, and 12 were a series of ports across the ducts for standard sampling methods.

Full identification of planes A-A, B-B, and C-C are given in figures 22, 23, and 24.

g. Sulfur Dioxide Distribution

A study of 12 west and 7 east plane A-A profiles of SO_2 shows that concentration varies widely from point to point. A typical SO_2 profile in figure 25 shows a point difference of 1000 ppm existed. The profile for a given test does not remain constant as highs and lows shift about causing the SO_2 concentration at a given point to vary. However, similar west-to-east and north-to-south trends were evident in profiles for both halves of the furnace. Figure 26 shows the average trend for the 12 west side tests.

FIGURE 22


PLANE A-A
(PLAN VIEW)
13'
19.5"
39"
39"
39"
46'
EAST
WEST
ARCH TUBES
DIVISION WALL
FRONT WALL OF FURNACE
SAMPLE POINTS
GAS FLOW UP
5 AW PROBE PATH
4 AE
5 AE
6 AE
7 AE
4 AW
6 AW
7 AW
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24

PLANE B-B

(ELEVATION)

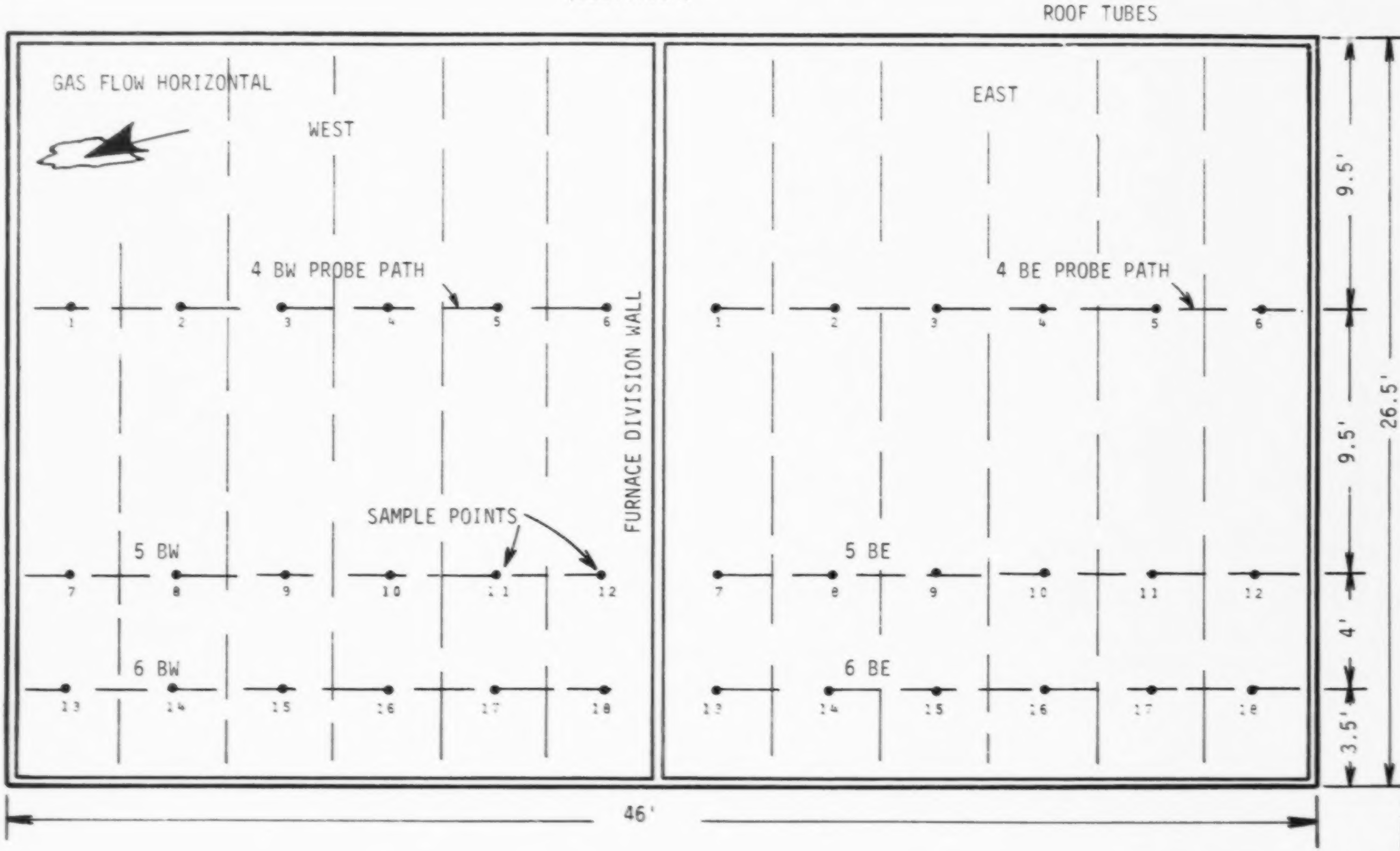
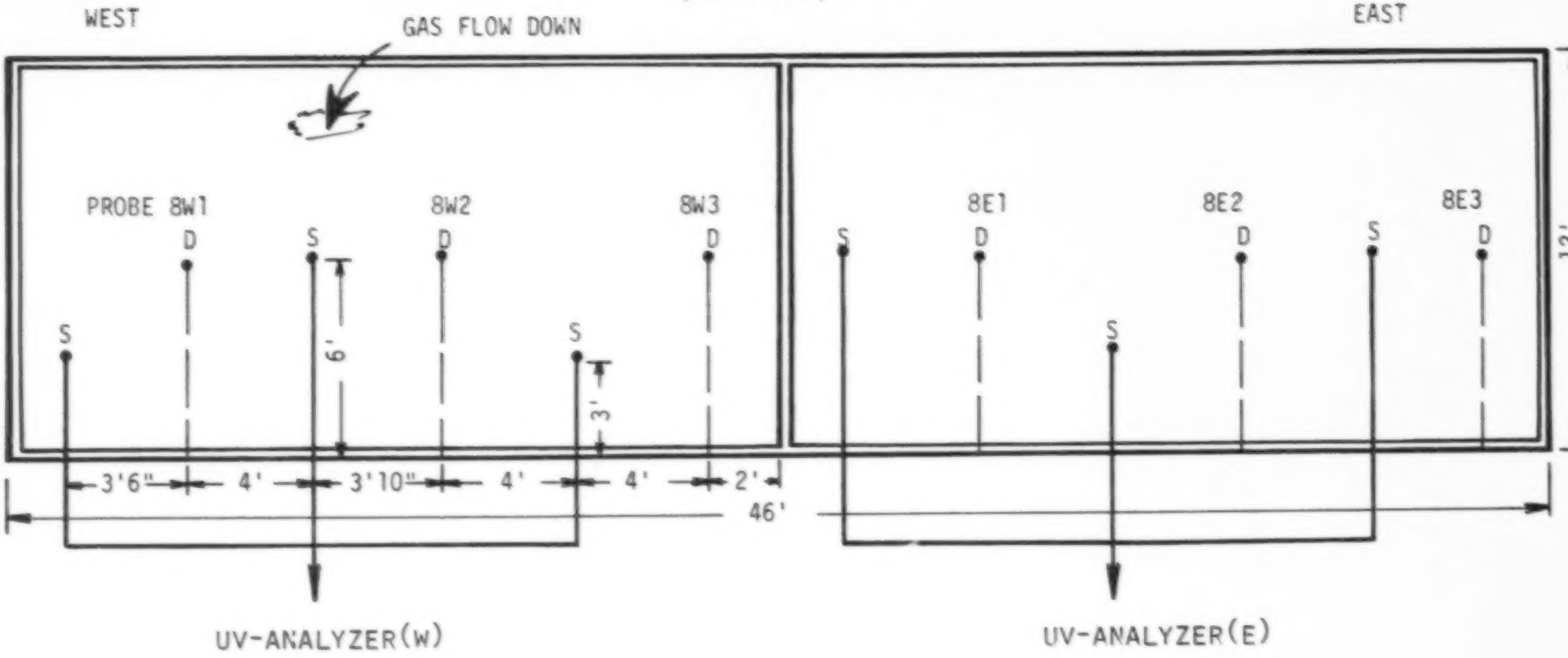

ROOF TUBES
GAS FLOW HORIZONTAL
WEST
EAST
4 BW PROBE PATH
4 BE PROBE PATH
FURNACE DIVISION WALL
SAMPLE POINTS
5 BW
6 BW
5 BE
6 BE
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
9.5'
9.5'
4'
3.5'
26.5'
46'

FIGURE 23

FIGURE 24

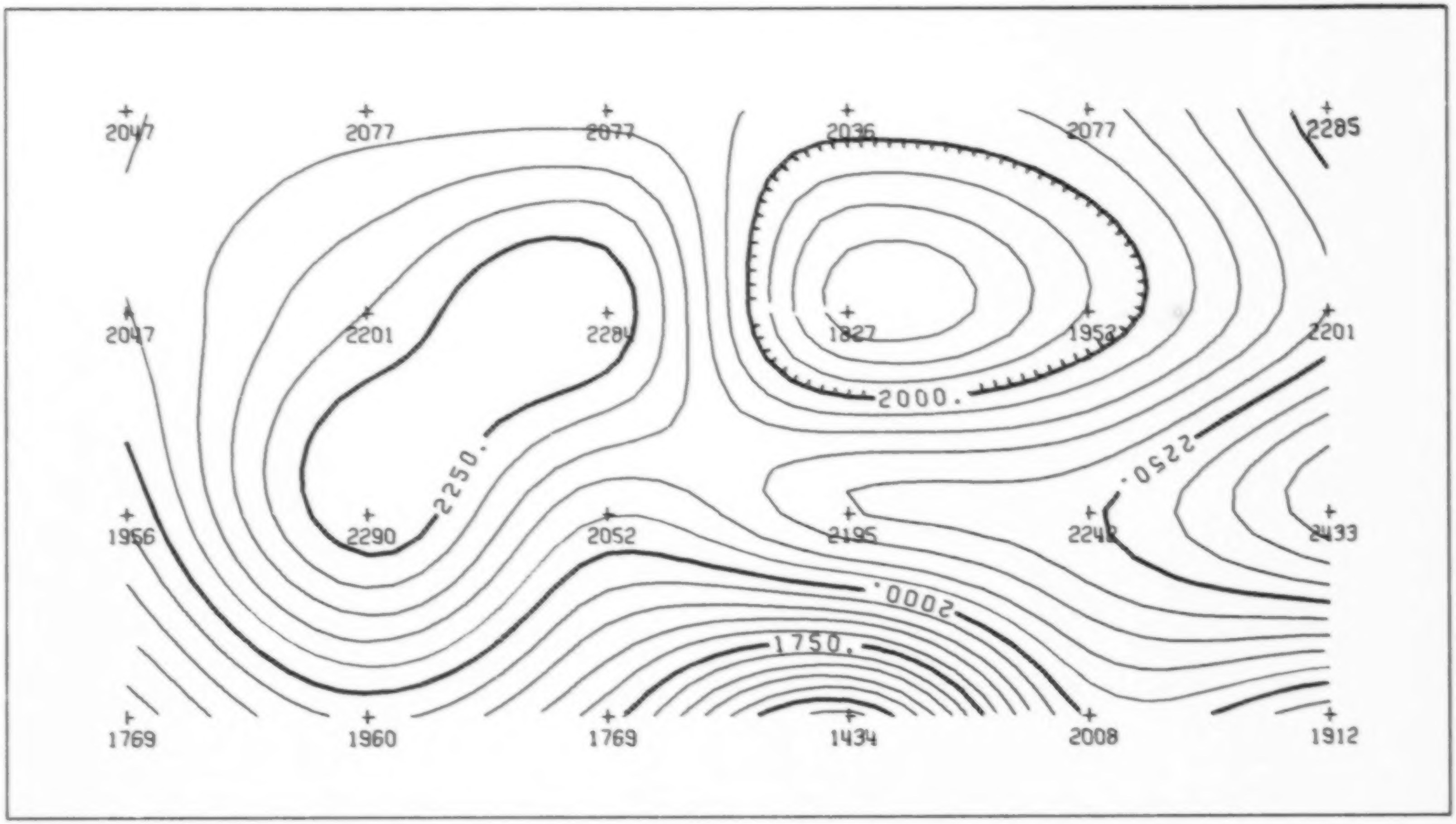
PLANE C-C

(PLAN VIEW)


WEST
GAS FLOW DOWN
EAST
PROBE 8W1
8W2
8W3
8E1
8E2
8E3
S
D
6'
3'
3'6"
4'
3'10"
4'
4'
2'
46'
12'
UV-ANALYZER(W)
UV-ANALYZER(E)

S - SO_2 SAMPLE POINT
D - DUST, TEMP, VEL. POINT

FIGURE 25



PLANE A-A WEST SIDE 3-16-70

SO2 DISTRIBUTION - INT. = 50 PPM

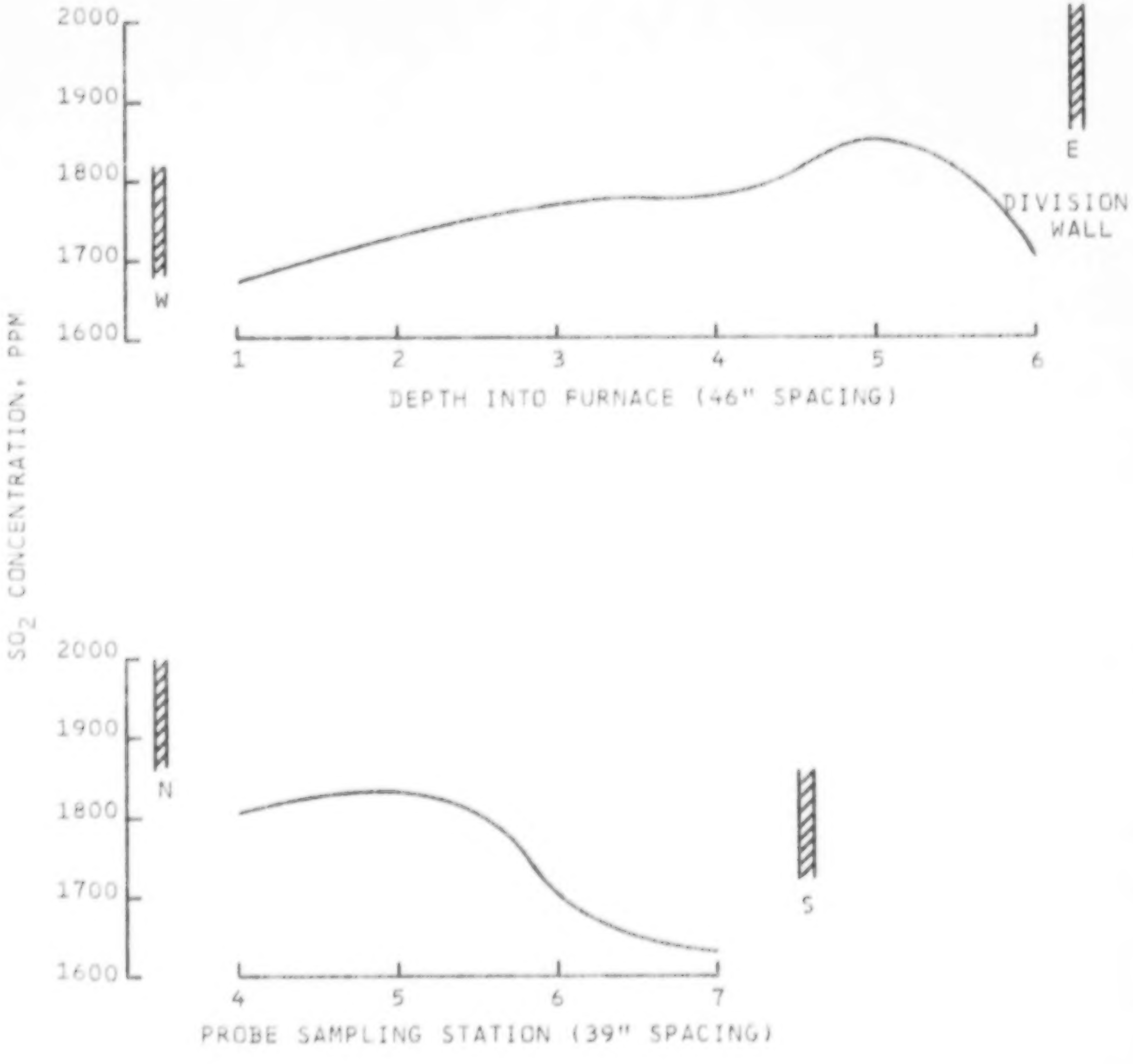
Test Conditions

Unit load 140 MW, excess air 25%
Plane A-A avg. SO_2 concentration 2048 ppm

FIGURE 26

SO_2 DISTRIBUTION PROFILE TRENDS

AVERAGE WEST-TO-EAST AND NORTH-TO-SOUTH
TRENDS FOR 12 WEST SIDE TESTS AT PLANE A-A



Early test program plans assumed that SO_2 distribution would be reasonably uniform. Therefore, the task of optimizing dust distribution appeared to require the determination of variable level combinations which would provide reasonably uniform dust distribution. Dust sampling got underway to provide initial information on sampling techniques during Phase I.

h. Dust Sampling

Sampling at planes A-A and C-C and chemical analysis of the dust, so called limestone modified fly ash mixture, provided initial information of the quantity of ash available for analysis and its chemical makeup. Fifteen minutes per sample point was used in Phase I. Obtaining isokinetic samples by proper manipulation of probes was achieved. Keeping probe dust tubes free of condensation products established maintenance procedures adopted for the rest of the program.

i. Oxygen Sampling

Traverses were made at the boiler outlet (plane C-C) and provided data for calculation of percent excess air. Portable analyzers proved suitable for measuring this important test variable since it enters stoichiometric calculations.

j. Calculational Procedures

The shakedown tests helped determine calculational procedures since these would vary according to sampling techniques. Computer programs were designed to provide test summary data and distribution plot of observing the effects of input variables.

Three methods for SO_2 removal computation were available but their use depended on different sampling procedures, as follows:

Calculation of SO_2 Removal

Method 1 - Data From Test

Coal rate, lbs./hr.
Percent Sulfur in coal - %
Percent excess combustion air - %EA
SO_2 concentration in flue gas - ppm by vol.
Wet flue gas density @ duct temp. - lbs./ft.^{3}
Pounds of flue gas per lb. of coal - lbs./lb.
Density of SO_2 @ duct temp. - lbs./ft.^{3}

$$\% \, SO_2 \text{ removal efficienty } = \left(\frac{SO_2 \text{ input} - SO_2 \text{ output}}{SO_2 \text{ input}}\right) \times 100$$

where: SO_2 input, ft^3/hr. = $\frac{\text{\% S coal} \times \text{lbs. coal/hr.} \times 64/32}{SO_2 \text{ density lbs./ft.}^3}$

and SO_2 output, ft^3/hr. = SO_2 ppm x $ft.^3$/hr. of wet gas

ft^3/hr. of wet gas = $\frac{\text{lbs. of wet gas/lb. coal} \times \text{lbs. coal/hr.}}{\text{wet gas density, lbs./ft.}^3}$

where lbs. of wet gas/lb. coal = $10.77 + \%\text{ EA} \times 9.89 + .013\ (9.89 + \%\text{ EA} \times 9.89) + .42 + .10 + .04$

Method 2 - Data from Test

Sulfur in coal - %

Coal rate - lbs./hr.

Ash in coal - %

Sulfur in fly ash and limestone products - %

Fly ash to bottom ash ratio - .80/.20

Sulfur in bottom ash - %

Flue gas density @ duct temp. - lb./$ft.^3$

Duct temperature - °F

% SO_2 removal efficiency = $\frac{\text{S removed in solids} \times 100}{\text{S input}}$

where: S input = % S coal x lb. coal/hr. = lb./hr.

S removed in solids = [(% S flyash x 0.8) + (% S bottom ash x 0.2)] x % ash in coal x lbs. coal/hr. = lbs./hr.

Material balance for sulfur:

S input = S output

where: S input = % S in coal x lbs. coal/hr. = lbs. S/hr.

S output = S in flue gas + S in solids

S in gas = $\frac{\text{ft.}^3 \text{ wet gas}}{\text{lb. coal}} \times SO_2 \text{ ppm} \times \frac{32}{64} \times SO_2 \text{ density @ duct temp.} \times \frac{\text{lbs. coal}}{\text{hour}}$

and S in solids as calculated above in lbs. S/lb. coal then total S output =

$\frac{(\text{lbs. S gas} + \text{lbs. S solids})}{\text{lb. coal}} \times \text{lbs. coal/hr.} = \text{lbs. S/hr.}$

Method 3 - Data from Test

Based on UV analyzer readings only

$$\% \ SO_2 \text{ removal efficiency} = 1 - \frac{D}{\left(\frac{A+B}{2}\right)} \times 100$$

where: A = SO_2 ppm reading after limestone injection is stopped
B = SO_2 ppm reading before limestone injection is started
D = SO_2 ppm reading during period of limestone injection

Method 1 requires the measurement of several variables as does Method 2 but the latter also includes an assumed split of fly ash and bottom ash plus need to analyze a small sample of bottom ash for sulfur content which may not be representative. Method 3 was selected because of its accuracy, continuity of measurement, and simplicity. Calibration gas was used daily to standardize the UV analyzers which were the only instruments used for Method 3. The SO_2 trace obtained during a typical startup and shutdown of limestone injection is shown in figure 27.

Reactant Utilization

The reactant in the case of limestone injection is calcium oxide, CaO, and is available after calcination when the CO_2 is liberated from $CaCO_3$. For perfect reaction, such as 1 stoichiometric, all the CaO is combined with SO_2 in sulfate form. No CaO would be found in a dust sample obtained from furnace gas downstream of the reaction zone. For this case 100% utilization would exist.

Practically, this condition is not achieved so percent utilization is defined as:

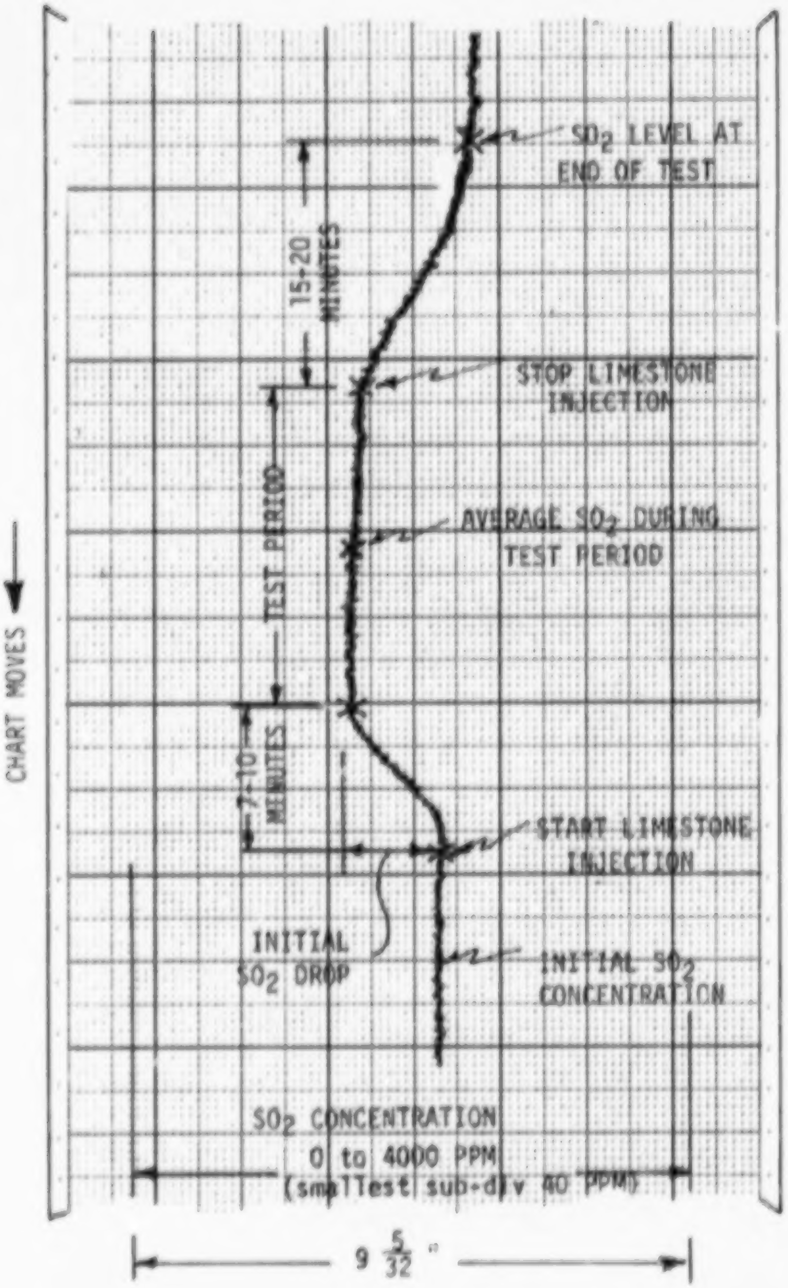
$$\% \text{ reactant utilized} = \frac{\text{wt. } SO_2 \cdot \text{MW reactant}}{\text{wt. reactant} \cdot \text{MW } SO_2} \cdot 100$$

where wt. SO_2 = % by weight SO_2 in sample
wt. reactant = % by weight reactant in sample
MW SO_2 = molecular weight SO_2 = 64.06
MW reactant = molecular weight reactant which for CaO = 56.08

Utilization of pulverized raw material, limestone or other, is even less and expressed by this equation.

$$\% \text{ limestone utilization} = \frac{\text{wt. \% of CaO utilized}}{\text{wt. \% of CaO in raw limestone}}$$

TYPICAL SO_2 CONCENTRATION CHANGE DURING STARTUP AND SHUTDOWN OF LIMESTONE INJECTION



The term deadburning is often referred to in this report. It concerns the degree of chemical unreactiveness that results from overheating limestone particles. Deadburned limestone particles exhibit physical changes in crystal structure such as reduced pore volume and surface area available for reaction with SO_2. Tests were devised to quantify this phenomenon, one being a fairly simple hydration test (see appendix C, procedure 6).

k. Injection Tests

A total of 35 injection tests with Fredonia limestone were completed during Phase I. Results are summarized in table 2. A computer printout for Test No. 1 is shown complete in figures 28 thru 34. These sheets are typical for all the tests in this phase. The summary sheets only are included for each of these tests and appear in appendix D.

Extensive study and analyses were conducted on these test results as carried out by TVA, the Control Systems Division of EPA and the latter's consulting engineering statistician. Multiple linear regression analysis on all test data failed to identify any statistically significant relationship between test variables and limestone distribution and SO_2 removal. Results of analyses upon selected tests indicated that no variable was significant for any of these Phase I tests.

It was assumed during planning stages of the test program that SO_2 distribution in the furnace would be reasonably uniform and,thus, limestone would require equally uniform distribution. The first analytical approach was to develop a Limestone Distribution Index called Sigma which was the standard deviation of the percent CaO in plane A-A and B-B fly ash samples. The derivation and an example for calculating Sigma is given in appendix E. Essentially, Sigma was a descriptive index which would indicate that for lower values of Sigma more uniform limestone distribution was achieved. Table 1 in appendix E includes a tabulation of this distribution index. Dust distribution was recognized as being one of the major variables even before testing. It was expected that some degree of control could be imposed on this distribution by manipulation of other variables such as injection angle, velocity and elevation.

The most significant information derived from the shakedown tests was recognition of an uncontrolled and previously unidentified variable. Different conditions existed between the east and west halves of the furnace which contributed to different limestone distributions and SO_2 removal efficiencies between these two halves. These variable conditions are now presumed to be caused by turbulence patterns in the boiler furnace.

The shakedown tests did reveal the differences in SO_2 removal between injection at lower rear and upper rear when Fredonia limestone and aragonite were injected. The percent SO_2 removal per unit stoichiometry plotted against the lime distribution index is shown in figure 35. The plot suggests the existence of a relationship between SO_2 removal and uniformity of limestone distribution. This was to be fully explored in Phase II. The results in figure 35 show that SO_2 removal increased by 8 percent (absolute) per unit stoichiometry for a given lime distribution as injection site was moved from lower rear to upper rear.

Table 8

Summary of Phase I Tests

Test No.	Injection Location	Stoich.	Plant Composite S in Coal, %	Injection Velocity, Ft./Sec.	Load MW	Excess Air, %		Initial SO_2 Level, ppm		Injection Angle	Particle Size No.	Limestone Utilization, %		Limestone Distribution Index*		SO_2 Removal, %	
						E	W	E	W			E	W	E	W	E	W
1	Lower Rear	1.86	2.4	130	140	26.5	24.3	1840	1840	0	4.0	11.7	11.7	5.4	6.5	15.1	10.8
2	Upper Rear	1.55	2.6	132	140	35.5	33.3	1600	1640	0	4.0	11.4	15.1	11.0	13.5	23.0	20.1
3	Upper Rear	1.84	2.2	59	143	27.3	20.0	1580	1580	0	4.5	6.8	7.7	16.6	14.1	15.2	7.3
4	Upper Rear	3.10	1.6	127	144	25.0	20.0	1140	1100	0	4.4	9.4	10.1	14.2	11.8	14.8	14.8
5	Upper Rear	3.68	1.4	67	142	18.0	16.7	1240	1240	0	4.2	7.2	6.3	18.2	16.3	14.8	14.8
6	Lower Rear	2.11	1.8	68	142	21.7	23.9	1480	1540	0	4.2	6.2	6.6	10.2	11.8	11.4	10.3
7	Lower Rear	2.30	2.0	130	140	18.3	19.2	2340	2120	0	4.6	5.2	6.3	11.0	8.8	11.0	9.4
8	Lower Rear	2.43	2.1	68	140	23.5	20.0	1900	1840	0	4.5	7.3	5.7	11.8	11.9	12.0	10.9
9	Upper Rear	1.47	2.5	940	140	14.1	18.0	2240	2160	0	4.7	10.4	9.0	15.0	12.7	13.2	14.2
10R2	Upper Rear	1.33	3.8	940	139	35.5	32.9	2400	2480	0	5.0	9.4	10.0	12.6	12.3	13.1	11.0
11	Front	1.53	3.3	195	139	29.6	31.3	2400	2440	0	5.0	7.9	8.6	14.2	12.7	4.7	11.0
12R3	Front	1.11	3.6	198	139	37.7	35.0	2300	2400	0	5.0	15.1	13.9	12.9	15.2	6.1	12.4
13	Front	1.76	2.2	101	142	37.7	37.7	1600	1600	0	4.7	7.1	9.1	17.7	15.8	14.1	12.9
14	Front	1.46	3.3	192	144	37.7	37.7	1800	1800	0	4.6	5.9	7.2	14.7	16.1	16.8	16.8
15	Upper Rear	1.75	2.1	945	142	40.0	33.3	1600	1520	0	4.8	9.9	12.8	11.8	14.1	27.3	26.2
16	Upper Rear	1.50	3.2	940	142	29.6	31.3	2680	2680	0	4.7	20.1	16.5	14.2	12.3	15.3	13.7
17	Upper Rear	1.01	3.5	131	142	29.6	31.3	2520	2400	+45	4.8	14.5	13.0	19.9	15.9	8.1	16.0
18	Upper Rear	1.77	2.4	131	141	29.6	37.3	2680	2480	+45	4.7	11.9	13.7	18.6	20.9	11.0	17.2
19	Upper Rear	1.16	3.0	132	142	38.2	39.1	2200	2200	-45	4.7	11.1	12.5	12.3	10.0	13.3	11.9
20	Upper Rear	1.69	3.0	132	142	38.2	39.1	2400	2160	-45	4.7	9.6	9.0	11.9	10.4	14.3	14.2
21	Upper Rear	0.87	2.6	134	138	16.0	16.6	2200	2080	-45	5.1	7.2	10.1	10.3	7.5	8.2	6.5
22	Upper Rear	1.76	1.7	131	140	25.0	15.4	1600	1680	0	4.8	11.8	11.1	18.0	13.6	17.3	15.0
23	Upper Rear	1.07	3.7	68	140	33.8	28.8	2720	2700	0	4.4	11.0	12.5	18.7	15.0	9.4	5.8
24	Upper Rear	1.70	3.2	67	139	32.9	39.1	2480	2480	-45	4.6	5.6	7.6	13.2	11.0	6.7	4.7
25	Upper Rear	1.29	4.0	68	116	22.1	23.5	3000	2920	0	5.2	6.7	5.1	13.2	11.8	8.7	8.9
26	Upper Rear	1.29	4.2	131	115	30.4	30.4	3200	3200	-45	4.8	7.9	8.7	12.3	10.3	4.3	5.7
27	Upper Rear	1.10	2.3	69	120	11.9	11.0	1960	2000	-45	5.7	10.2	11.3	8.1	8.1	8.7	11.5
28	Upper Rear	1.13	2.5	135	117	26.5	28.2	1800	1900	0	5.7	12.5	13.8	12.0	11.2	11.1	11.9
6A	Lower Rear	1.19	2.6	69	137	22.8	23.5	2400	2360	0	4.4	9.5	8.6	13.4	16.7	6.9	4.3
7A	Lower Rear	1.72	2.3	132	139	17.3	21.6	2080	1960	0	4.8	6.9	6.1	4.9	9.6	11.2	10.9
8A	Lower Rear	2.01	2.4	68	140	22.1	23.5	2080	2000	0	4.5	6.5	7.4	7.0	11.5	11.2	10.8
2A	Upper Rear	1.11	2.1	133	138	35.5	32.1	1620	1520	0	5.1	10.3	12.2	13.7	13.4	11.3	17.1
4A	Upper Rear	1.39	1.9	132	139	27.3	20.7	1760	1660	0	4.3	6.9	8.0	13.0	15.4	14.2	21.7
29	Upper Rear	0.86	1.7	136	78	27.0	28.0	1560	1440	0	5.0	12.3	17.0	9.0	8.5	13.0	14.5
1A	Lower Rear	1.44	2.7	130	138	25.4	29.2	2440	2480	0	5.1	7.4	6.1	4.1	11.4	10.9	8.6

*See Appendix E

FIGURE 28

```
        TENNESSEE VALLEY AUTHORITY - DIVISION OF POWER PRODUCTION

              SULFUR OXIDE REMOVAL FROM POWER PLANT STACK GAS

         FULL-SCALE LIMESTONE INJECTION TESTS AT SHAWNEE UNIT 10

TEST NO.1        DATE:           MAY 12, 1970

TEST CONDITIONS
   UNIT LOAD, MW                                       140
   BOILER LOAD, MLBS/HR                                985
   COAL RATE, LBS/HR                                122039.
   LIMESTONE RATE, LBS/LBCOAL                         0.147
   INJECTION VELOCITY, FT/SEC                          130
   INJECTION ANGLE,DEGREES                               0
   INJECTION ELEVATION                            LOWER REAR
   LIMESTONE TYPE, BCR NO.                            2061
   PARTICLE SIZE, MICRONS                              4.0
   STOICHIOMETRY                                      1.86
   COAL TYPE,CONTRACT NO.                            43T15
   EXCESS AIR,PERCENT -       WEST    24.3     EAST    26.5

COAL ANALYSIS - PROXIMATE          ACTUAL

             VOLATILE    FIXED
  MOISTURE    MATTER     CARBON         ASH       SULFUR
    13.0       31.1       44.3          11.6        2.4

COAL ANALYSIS - ULTIMATE

  HYDROGEN  NITROGEN     CARBON     SULFUR       ASH    MOISTURE
     4.06      1.21       64.83       2.40      11.60      13.00

% LIMESTONE UTILIZED, BOILER OUTLET - WEST  11.7 EAST  11.3

SO2 REMOVAL EFFICIENCY,%,BOILER OUTLET
                METHOD 1       METHOD 2       METHOD 3
               WEST  EAST    WEST  EAST     WEST  EAST
               12.2  17.6    13.8  14.1     10.7  15.0

SO2 MATERIALS BALANCE          INPUT,LBS/HR    OUTPUT,LBS/HR     DIFFERENCE
                                  5858.           6640.              782.

CAO MATERIALS BALANCE            10052.           6238.            -3814.

THEORETICAL CAO IN DUST,%,SAMPLING PLANE           41.52

THEORETICAL FLY ASH,GRNS/CUFT,SAMPLING PLANE-  WEST   4.71  EAST   4.64
```

FIGURE 29

```
   TEST NO.  1      DATE:           MAY 12, 1970  INPUT DATA

        1               MAY 12, 1970  ACTUAL  1  1 0.00294    1.00    0.41

        130  985 4.0 2061   0                LOWER REAR        43T15   140

        13.0  31.1  44.3  11.6   2.4

      C. RATE    STD    S BA    L/C   C BA C MECH C ELEC S MECH S ELEC
     122039.   1.86   0.83   0.15  14.51  45.92  13.63   2.62   2.42

          EXA    T BO    S FA   C FA    SOB    SOD    SOA DELS B DELS E
     WEST  24.3   715.    4.55  33.94  1840.  1560.  1720.   140.   240.
     EAST  26.5   728.    4.56  35.29  1840.  1520.  1760.   220.   320.

        24  TEST POINTS,SAMPLING PLANE A-A,WEST SIDE

           MV         VP       STAT    T SAMP      DUST       CAO        SO2   SO2 PP
        11.50       0.21     -6.00   160.00       0.51      61.54       0.63  1840.00
        11.30       0.24     -6.00   160.00       0.67      45.44       0.78  1840.00
         9.80       0.08     -6.00   160.00       0.09      46.13       1.23  1840.00
        12.00       0.13     -6.00   160.00       0.49      41.55       1.52  1840.00
         9.00       0.08     -6.00   160.00       0.44      45.61       1.54  1840.00
         8.30       0.12     -6.00   160.00       0.10      44.97       1.80  1840.00
        12.00       0.22     -6.00   160.00       0.56      54.18       0.76  1840.00
        13.00       0.23     -6.00   160.00       0.76      51.73       0.88  1840.00
        13.50       0.22     -6.00   160.00       0.59      55.85       1.33  1840.00
        13.50       0.23     -6.00   160.00       0.49      46.90       0.94  1840.00
        13.50       0.24     -6.00   160.00       0.21      57.30       1.07  1840.00
        12.50       0.17     -6.00   160.00       0.03      62.93       0.44  1840.00
        10.00       0.06     -6.00   160.00       0.35      48.43       2.16  1840.00
        11.50       0.05     -6.00   160.00       0.15      45.46       2.11  1840.00
        12.00       0.06     -6.00   160.00       0.29      49.48       1.75  1840.00
        12.00       0.09     -6.00   160.00       0.18      46.48       1.41  1840.00
        12.00       0.15     -6.00   160.00       0.50      49.93       1.22  1840.00
        11.50       0.09     -6.00   160.00       0.05      68.59       1.26  1840.00
         9.80       0.02     -6.00   160.00       0.61      49.25       1.32  1840.00
        11.00       0.05     -6.00   160.00       0.37      50.09       0.78  1840.00
        11.40       0.06     -6.00   160.00       0.61      49.37       0.95  1840.00
        11.50       0.10     -6.00   160.00       1.05      50.19       0.48  1840.00
        11.50       0.11     -6.00   160.00       0.40      54.69       0.63  1840.00
        11.00       0.10     -6.00   160.00       0.09      61.92       0.63  1840.00

        AVERAGE CAO IN DUST,%,SAMPLING PLANE             51.58
```

FIGURE 30

```
TEST NO.  1      DATE:            MAY 12, 1970

24  TEST_POINTS,SAMPLING PLANE A-A,EAST SIDE

     MV          VP        STAT     T SAMP       DUST         CAO          SO2     SO2 PP
    9.50       0.07       -6.00     160.00       0.04        42.41        0.65    1840.00
    9.50       0.06       -6.00     160.00       0.44        55.73        0.81    1840.00
    9.50       0.07       -6.00     160.00       0.25        59.92        1.84    1840.00
    9.80       0.10       -6.00     160.00       0.31        54.42        0.68    1840.00
   10.00       0.12       -6.00     160.00       0.69        47.72        0.75    1840.00
    8.80       0.09       -6.00     160.00       1.17        47.92        0.88    1840.00
   11.50       0.11       -6.00     160.00       0.09        54.78        0.88    1840.00
   11.80       0.04       -6.00     160.00       0.27        54.77        0.87    1840.00
   12.00       0.15       -6.00     160.00       0.30        60.11        0.85    1840.00
   12.50       0.16       -6.00     160.00       0.12        50.35        0.60    1840.00
   12.50       0.17       -6.00     160.00       0.26        55.47        0.47    1840.00
   11.80       0.19       -6.00     160.00       0.59        48.81        1.32    1840.00
   11.00       0.11       -6.00     160.00       0.59        49.31        0.71    1840.00
   11.50       0.11       -6.00     160.00       0.21        53.67        0.85    1840.00
   11.30       0.14       -6.00     160.00       0.62        53.46        1.12    1840.00
   11.50       0.11       -6.00     160.00       0.17        48.18        1.03    1840.00
   11.50       0.08       -6.00     160.00       0.04        46.26        0.85    1840.00
   11.00       0.15       -6.00     160.00       0.58        40.93        1.33    1840.00
    9.30       0.05       -6.00     160.00       0.43        47.03        1.27    1840.00
    9.80       0.08       -6.00     160.00       0.54        48.81        1.18    1840.00
   10.00       0.06       -6.00     160.00       0.41        51.94        1.09    1840.00
   10.50       0.05       -6.00     160.00       0.28        44.52        0.82    1840.00
   10.80       0.06       -6.00     160.00       0.29        42.13        1.14    1840.00
   10.00       0.05       -6.00     160.00       0.43        42.11        1.26    1840.00

    AVERAGE CAO IN DUST,%,SAMPLING PLANE                     50.03
```

FIGURE 31

```
TEST NO.  1      DATE:            MAY 12, 1970
   SAMPLING PLANE A-A,WEST SIDE

                     LIMESTONE DISTRIBUTION INDEX

  SAMPLING      SO2   CAO GR LDG VELOCITY     SO2         CAO   THEORET CAO
  LOCATION      PPM   GRNS/CUFT   FT/SEC   CUFT/SEC  GRNS/SEC   GRNS/SEC

      1        1840.     2.15      67.1     0.0235       27.        23.
      2        1840.     1.94      71.3     0.0253       27.        25.
      3        1840.     0.44      39.3     0.0153        4.        15.
      4        1840.     1.80      53.6     0.0182       18.        18.
      5        1840.     2.06      38.2     0.0157       18.        16.
      6        1840.     0.37      45.6     0.0197        4.        20.
      7        1840.     2.06      69.7     0.0237       27.        24.
      8        1840.     2.68      73.2     0.0236       34.        24.
      9        1840.     2.33      72.6     0.0228       29.        23.
     10        1840.     1.59      74.2     0.0233       20.        23.
     11        1840.     0.81      75.8     0.0238       11.        24.
     12        1840.     0.15      62.1     0.0205        2.        21.
     13        1840.     2.07      34.2     0.0132       15.        13.
     14        1840.     0.96      32.7     0.0115        6.        11.
     15        1840.     1.87      36.4     0.0124       13.        12.
     16        1840.     0.89      44.6     0.0152        7.        15.
     17        1840.     2.05      57.5     0.0196       22.        20.
     18        1840.     0.36      43.9     0.0154        3.        15.
     19        1840.     6.33      19.6     0.0076       26.         8.
     20        1840.     2.56      32.3     0.0116       16.        12.
     21        1840.     3.85      35.8     0.0126       26.        13.
     22        1840.     5.23      46.3     0.0162       46.        16.
     23        1840.     2.07      48.6     0.0170       19.        17.
     24        1840.     0.55      45.6     0.0164        5.        16.

   AVERAGE CAO GR LDG,GRNS/CUFT =    1.97

      R = 0.230

      T = 0.848

      AVG. % OFF THEORETICAL      54

      SIGMA (% OFF)               58

                        SUM      112

      CHI-SQUARE (% OFF)         198

      SIGMA(% CAO IN DUST)          6.6

      AVG.STOICH.DEVIATION        56.80

FLY ASH LOADING,GRNS/CUFT,AT STANDARD CONDITIONS - - AVERAGE=  1.96
  1.34        2.33       0.51       2.53       2.45       0.45
  1.74        2.50       1.84       1.80       0.61       0.09
  2.21        1.15       1.91       1.02       2.06       0.16
  6.52        2.56       3.95       5.19       1.72       0.34
```

FIGURE 32

TEST NO. 1 DATE: MAY 12, 1970
SAMPLING PLANE A-A,WEST SIDE

EFFECTIVE STOICHIOMETRY

SAMPLING LOCATION	SO2 CUFT/SEC	CAO GRNS/SEC	RATIO CAO/SO2	STOICHIO QUAN.CAC	SO2 RECOVERED FRACTION	SO2 RECOVERED CUFT	SO2 REMOVAL EFFICIENCY
1	0.0235	27.	1169.	1.069	0.355	0.008	1.0
2	0.0253	27.	1054.	0.964	0.327	0.008	1.4
3	0.0153	4.	238.	0.217	0.085	0.001	0.5
4	0.0182	18.	978.	0.894	0.307	0.006	2.9
5	0.0157	18.	1117.	1.022	0.342	0.005	3.0
6	0.0197	4.	199.	0.182	0.072	0.001	0.6
7	0.0237	27.	1120.	1.024	0.343	0.008	1.3
8	0.0236	34.	1459.	1.334	0.421	0.010	2.0
9	0.0228	29.	1267.	1.158	0.378	0.009	2.4
10	0.0233	20.	864.	0.790	0.277	0.006	1.4
11	0.0238	11.	443.	0.405	0.153	0.004	0.7
12	0.0205	2.	80.	0.074	0.030	0.001	0.0
13	0.0132	15.	1127.	1.031	0.345	0.005	4.0
14	0.0115	6.	520.	0.476	0.177	0.002	1.9
15	0.0124	13.	1014.	0.927	0.316	0.004	2.9
16	0.0152	7.	483.	0.442	0.166	0.003	1.2
17	0.0196	22.	1116.	1.021	0.342	0.007	2.2
18	0.0154	3.	195.	0.178	0.071	0.001	0.3
19	0.0076	26.	3439.	3.145	0.725	0.006	7.4
20	0.0116	16.	1394.	1.275	0.407	0.005	1.7
21	0.0126	26.	2092.	1.913	0.544	0.007	3.2
22	0.0162	46.	2844.	2.601	0.656	0.011	2.2
23	0.0170	19.	1126.	1.029	0.344	0.006	1.0
24	0.0164	5.	296.	0.271	0.105	0.002	0.2

EFFECTIVE STOICHIOMETRY = 0.934 AVERAGE POINT STOICHIOMETRY = 0.977

TEMPERATURES,DEGREES FAHRENHEIT AVERAGE = 2119.

2126.	2096.	1867.	2201.	1742.	1631.
2201.	2351.	2426.	2426.	2426.	2276.
1897.	2126.	2201.	2201.	2201.	2126.
1867.	2052.	2111.	2126.	2126.	2052.

DUST LOADING,GRNS/CUFT,AT STANDARD CONDITIONS

3.49	4.27	0.95	4.33	4.51	0.82
3.80	5.19	4.17	3.39	1.42	0.24
4.28	2.11	3.77	1.91	4.11	0.52
12.85	5.12	7.80	10.43	3.79	0.88

GAS VELOCITY,FT/SEC AVERAGE = 50.8

67.1	71.3	39.3	53.6	38.2	45.6
69.7	73.2	72.6	74.2	75.8	62.1
34.2	32.7	36.4	44.6	57.5	43.9
19.8	32.3	35.8	46.3	48.6	45.6

LIMESTONE UTILIZED,PERCENT

0.9	1.5	2.3	3.2	3.0	3.5
1.2	1.5	2.1	1.8	1.6	0.6
3.9	4.1	3.1	2.7	2.1	1.6
2.3	1.4	1.7	0.8	1.0	0.9

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FIGURE 33

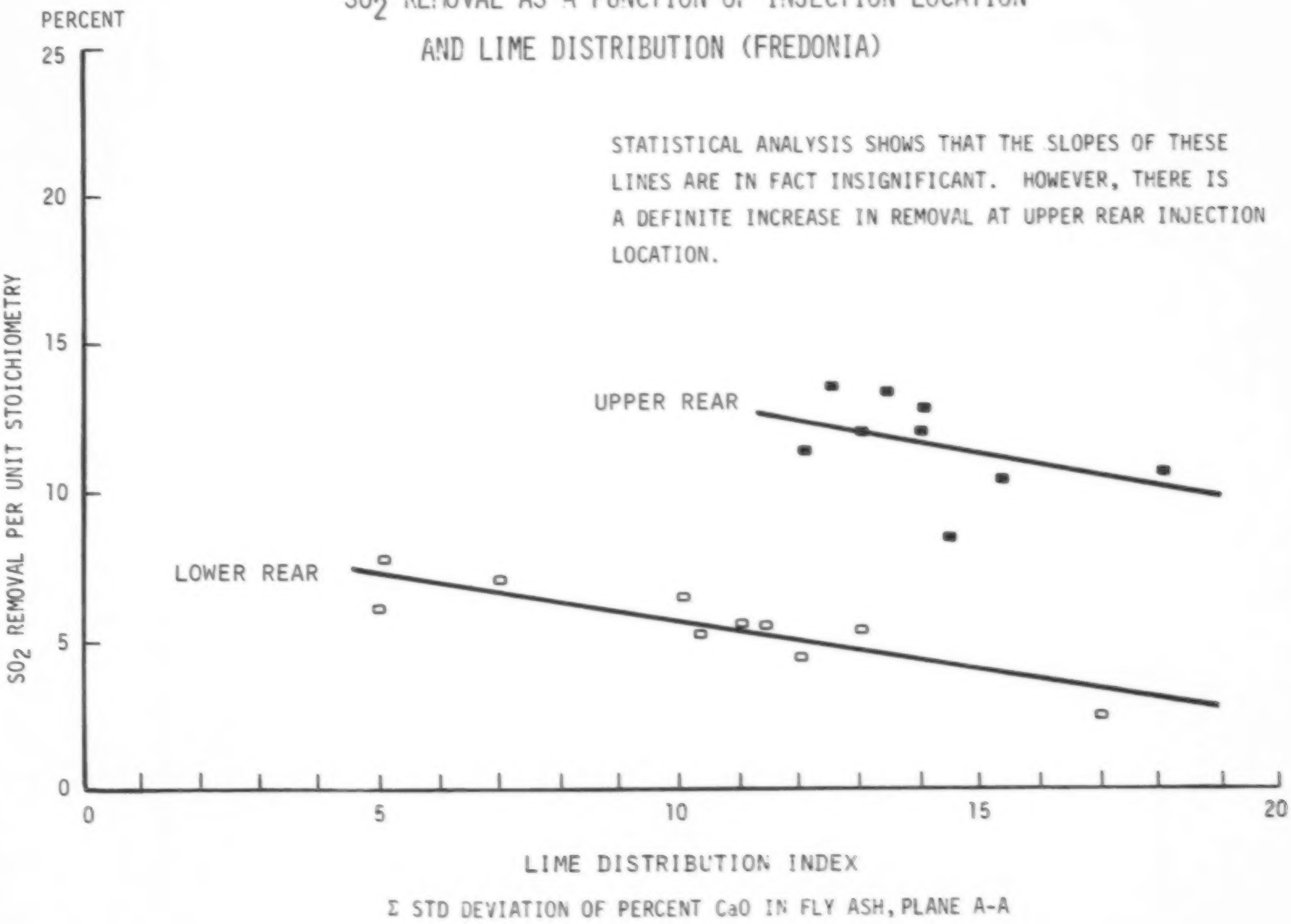
```
TEST NO.  1      DATE:            MAY 12, 1970
   SAMPLING PLANE A-A,EAST SIDE

                        LIMESTONE DISTRIBUTION INDEX

    SAMPLING        SO2    CAO GR LOG VELOCITY     SO2         CAO    THEORET CAO
    LOCATION        PPM    GRNS/CUFT   FT/SEC   CUFT/SEC  GRNS/SEC   GRNS/SEC

         1        1840.       0.19       36.4     0.0144        1.         15.
         2        1840.       2.95       33.7     0.0134       21.         14.
         3        1840.       1.67       36.4     0.0144       13.         15.
         4        1840.       1.59       43.9     0.0171       15.         16.
         5        1840.       3.68       48.4     0.0186       37.         20.
         6        1840.       5.38       40.3     0.0168       49.         18.
         7        1840.       0.47       48.6     0.0170        4.         18.
         8        1840.       2.34       29.5     0.0102       13.         11.
         9        1840.       1.48       57.5     0.0196       16.         21.
        10        1840.       0.49       60.3     0.0199        5.         21.
        11        1840.       1.13       62.1     0.0205       13.         22.
        12        1840.       2.09       64.4     0.0222       25.         23.
        13        1840.       2.71       47.9     0.0173       25.         18.
        14        1840.       1.07       48.6     0.0170       10.         18.
        15        1840.       2.77       54.5     0.0193       29.         20.
        16        1840.       0.78       48.6     0.0170        7.         18.
        17        1840.       0.21       41.4     0.0145        2.         15.
        18        1840.       2.32       45.6     0.0164       21.         17.
        19        1840.       2.65       30.5     0.0123       18.         13.
        20        1840.       2.78       39.3     0.0153       23.         16.
        21        1840.       2.61       34.2     0.0132       19.         14.
        22        1840.       1.70       31.8     0.0118       11.         12.
        23        1840.       1.53       35.1     0.0128       11.         14.
        24        1840.       2.43       31.3     0.0120       16.         13.

    AVERAGE CAO GR LOG,GRNS/CUFT =    1.96

       R = 0.226

       T = 0.848

       AVG. % OFF THEORETICAL      48

       SIGMA (% OFF)               37

                         SUM       85

       CHI-SQUARE (% OFF)        153

       SIGMA(% CAO IN DUST)         5.4

       AVG.STOICH.DEVIATION      51.32

FLY ASH LOADING,GRNS/CUFT,AT STANDARD CONDITIONS - - AVERAGE=  2.01
   0.26        2.34        1.12        1.33        4.03        5.84
   0.39        1.93        0.98        0.48        0.91        2.19
   2.79        0.92        2.41        0.83        0.24        3.35
   2.98        2.91        2.41        2.12        2.11        3.34
```

FIGURE 34

```
TEST NO. 1      DATE:          MAY 12, 1970
   SAMPLING PLANE A-A,EAST SIDE

                      EFFECTIVE STOICHIOMETRY

SAMPLING     SO2       CAO     RATIO   STOICHIO SO2 RECOVERED  SO2 REMOVAL
LOCATION  CUFT/SEC GRNS/SEC CAO/SO2  QUAN.CAO FRACTION  CUFT    EFFICIENCY

    1      0.0144        1.    103.    0.094    0.038   0.001       0.1
    2      0.0134       21.   1604.    1.467    0.452   0.006       1.9
    3      0.0144       13.    907.    0.830    0.288   0.004       2.2
    4      0.0171       15.    864.    0.790    0.277   0.005       0.9
    5      0.0186       37.   1998.    1.827    0.527   0.010       2.5
    6      0.0168       49.   2922.    2.672    0.666   0.011       4.3
    7      0.0170        4.    254.    0.232    0.091   0.002       0.3
    8      0.0102       13.   1273.    1.164    0.380   0.004       1.6
    9      0.0196       16.    806.    0.737    0.261   0.005       0.9
   10      0.0199        5.    265.    0.242    0.095   0.002       0.3
   11      0.0205       13.    614.    0.562    0.206   0.004       0.4
   12      0.0222       25.   1137.    1.040    0.347   0.008       2.5
   13      0.0173       25.   1475.    1.349    0.425   0.007       1.7
   14      0.0170       10.    580.    0.530    0.195   0.003       0.7
   15      0.0193       29.   1503.    1.375    0.431   0.008       2.5
   16      0.0170        7.    421.    0.385    0.146   0.002       0.7
   17      0.0145        2.    112.    0.102    0.041   0.001       0.2
   18      0.0164       21.   1263.    1.155    0.377   0.006       3.3
   19      0.0123       18.   1439.    1.316    0.417   0.005       3.1
   20      0.0153       23.   1508.    1.379    0.432   0.007       2.9
   21      0.0132       19.   1416.    1.295    0.412   0.005       2.4
   22      0.0118       11.    923.    0.844    0.292   0.003       1.4
   23      0.0128       11.    834.    0.763    0.268   0.003       1.8
   24      0.0120       16.   1319.    1.207    0.390   0.005       3.2

EFFECTIVE STOICHIOMETRY = 0.942     AVERAGE POINT STOICHIOMETRY = 0.973

TEMPERATURES,DEGREES FAHRENHEIT               AVERAGE =  2008.
 1820.      1820.      1820.      1867.      1897.      1711.
 2126.      2171.      2201.      2276.      2276.      2171.
 2052.      2126.      2096.      2126.      2126.      2052.
 1789.      1867.      1897.      1973.      2022.      1897.

DUST LOADING,GRNS/CUFT,AT STANDARD CONDITIONS
   0.45       5.30       2.79       2.92       7.70      11.22
   0.85       4.28       2.47       0.97       2.04       4.29
   5.50       1.99       5.17       1.61       0.44       5.68
   5.63       5.69       5.02       3.81       3.64       5.76

GAS VELOCITY,FT/SEC                           AVERAGE =   43.8
   36.4       33.7       36.4       43.9       48.4       40.3
   48.6       29.5       57.5       60.3       62.1       64.4
   47.9       48.6       54.5       48.6       41.4       45.6
   30.5       39.3       34.2       31.8       35.1       31.3

LIMESTONE UTILIZED,PERCENT
    1.3        1.3        2.7        1.1        1.4        1.6
    1.4        1.4        1.2        1.0        0.7        2.4
    1.3        1.4        1.8        1.9        1.6        2.8
    2.4        2.1        1.8        1.6        2.4        2.6
```

FIGURE 35

SO$_2$ REMOVAL AS A FUNCTION OF INJECTION LOCATION AND LIME DISTRIBUTION (FREDONIA)



STATISTICAL ANALYSIS SHOWS THAT THE SLOPES OF THESE LINES ARE IN FACT INSIGNIFICANT. HOWEVER, THERE IS A DEFINITE INCREASE IN REMOVAL AT UPPER REAR INJECTION LOCATION.

The effects of limestone injection on Unit 10 operation during Phase I revolved on keeping the heat transfer surfaces clean by adequate soot blowing and checking out procedures for sampling that would require close cooperation between test personnel and boiler operators.

4. CONCLUSIONS

a. The Shawnee coal supply varies widely so consequently wide variations in sulfur content were experienced. It was recognized that this might have been the source of trouble in trying to obtain meaningful correlations of test variables with SO_2 removal, particularly with stoichiometry. This led to the conclusion that increased coal sampling frequency and reduction in test run duration should be part of future test procedures.

b. Analysis of hydration data indicated that limestone injected at lower rear showed deadburning or loss of reactivity occurred to a greater extent than stone injected at the upper rear of the furnace. This deadburning resulted in lower SO_2 removal and exists because of particle exposure to higher gas temperatures and for longer time periods. This confirmed analytical work that showed injection at lower temperature with resulting shorter residence time was better than injection at higher temperature and longer residence time.

c. Evidence that difference existed between the two halves of the furnace pointed to the probable strong effect of furnace gas turbulence on such matters as dust distribution and the possible influence of operating parameters such as excess air, burner firing patterns, load, and others.

d. Statistical analysis of these preliminary data showed the necessity for this type of approach because of the numerous variables involved whether they were controlled or uncontrolled.

e. The moveable, water-cooled probes in the plane A-A appeared adequate for the sampling program but that some other techniques would be required to get evidence of instantaneous or millisecond duration of limestone dust distribution.

f. The effects of limestone injection on the boiler showed greater attention would be required on soot blowing, particularly in the reheater, and to sluicing operations. The observation of reheater plugging provided the first evidence at Shawnee that long term injection might pose serious problems for the process.

D. PHASE II, DUST DISTRIBUTION STUDIES

1. OBJECTIVES

The major objective of Phase II was to determine the quality of limestone distribution in the furnace gas and the effect of this distribution on SO_2 removal.

The results of Phase I pointed out that factors of combustion turbulence plus unknown and uncontrolled variables associated with turbulence were influencing dust distribution. The Phase II program was designed to identify and, if possible, to control those variables. Several boiler operating variables were suspected of being the uncontrolled influence on dust distribution and on temperature and velocity fluctuations. Among these variables were furnace slagging conditions, soot blowing, pulsations in pulverizer operation, unbalanced pulverizer loading, and secondary air damper setting.

2. APPROACH

A series of tests were planned to determine the effect on dust distribution of as many of the above variables as possible. The response variables to be measured were temperature, velocity, and lime dust concentration (as percent CaO in fly ash) profiles at plane A-A while injecting at upper rear, lower rear, front, or upper rear-front combinations. The use of dolomites, precalcined stones, hydrated lime, and catalyst promoters were not considered since none of the support projects predicted any significant improvement in performance over limestone (see appendix I). Fredonia limestone was used during Phase II. Study of dust distribution by means of holography was undertaken by Control Systems Division of EPA in a separate research contract in hope that instantaneous dust distribution could be observed. There was also some work by TVA on a dust tape sampler fitted to one probe.

The approach was to obtain data from plane A-A probes such that profiles would possibly reveal influences on dust distribution caused by manipulating the input variables. There was no sootblowing or sluicing allowed during sampling periods thus reducing pulsations. The results of this program in Phase II will now be discussed.

3. RESULTS

a. Effects of Excess Air and Slagging Conditions

The first tests were designed to show the effect of excess air on furnace temperature and slagging, a typical example of which appears in figure 36. The average gas temperature leaving the furnace increased 150-200°F as excess air was reduced from 20% to 12.5% by reducing total air flow yet holding load constant. Both halves of the furnace were balanced as equally as possible by burner adjustments. The net effect of changing excess air on mean gas velocity may be slight since reduced specific volume of the gas is compensated by increased mass flow. Little effect of excess air on dust distribution was observed.

The removal of slag from furnace walls by the deslagging wall blowers resulted in a decrease of 100 to 200 °F in plane A-A average gas temperature. A change of 200 °F could be expected to affect the degree of deadburning of lime and, in turn, the percent of SO_2 removal. Excess air can be controlled during testing but furnace slagging cannot. Therefore, slagging is one uncontrolled variable which may have contributed to unexplained fluctuation in SO_2 removal during Phase I.

b. Short-Term (Minute and Hourly) Temperature and Velocity Profile Changes

In order to determine the effect of variables on furnace turbulence, it was first necessary to determine whether conditions could be maintained constant long enough to obtain a constant turbulence pattern. Figures 37 through 41 are representative samples of temperature profiles from a total of 18 sets run from 5 minutes to 7 hours apart on the same day. Close inspection of these profiles reveals that the patterns are essentially the same. This was true for all temperature and velocity profiles on both east and west furnaces for the day. Minor adjustments to secondary air dampers helped maintain a constant 3.5% oxygen at the boiler outlet (plane C-C).

c. Velocity and Temperature Profile Changes with Secondary Air Damper Settings

The next series of profiles were run with the objective of determining the effect of secondary air damper changes on velocity and temperature patterns. Figures 42 through 44 are representative temperature profiles from a set of ten that were obtained before damper changes, and figures 45 through 47 are representative of eight profiles obtained after damper changes were made. The distinct change which took place is obvious by comparison of figures 44 and 45. The same effect occurred with velocity profiles. These patterns offer firm evidence that secondary air damper settings definitely influence turbulence patterns in the boiler furnace. Other related fluctuations in the firing system such as pulverizer pulsations or imbalanced pulverizer operation can be expected to have similar but smaller effects since 10-15% of the total air enters through pulverizers.

d. Short-Term (Hourly) Dust Distribution Changes

Having determined the characteristics of temperature and velocity fluctuations, the next series of tests were directed toward establishing the nature of dust profile changes. The first series were concerned with hourly fluctuations on a given day with limestone being injected horizontally (0° angle) through lower rear, upper rear, and finally the front nozzles. Figures 48 through 53 show profiles of % CaO in dust samples obtained from fly ash withdrawn from the west furnace approximately one hour apart on the same day. The pattern is similar for all profiles: CaO concentrations are generally high in the right half of the west furnace and taper off to lower values on the left half. (The theoretical percent CaO in fly ash which should be found, calculated from the injection rate for ash in coal, is 46.1 percent. The average percent CaO found for figures 48 through 53 are 46, 46, 45, 46, 48, and 47 percent respectively.) Although a different pattern is observed in the east furnace, the conclusion is the same: if boiler load, coal, and burner settings are held constant the CaO concentration profiles for a given day remain relatively constant.

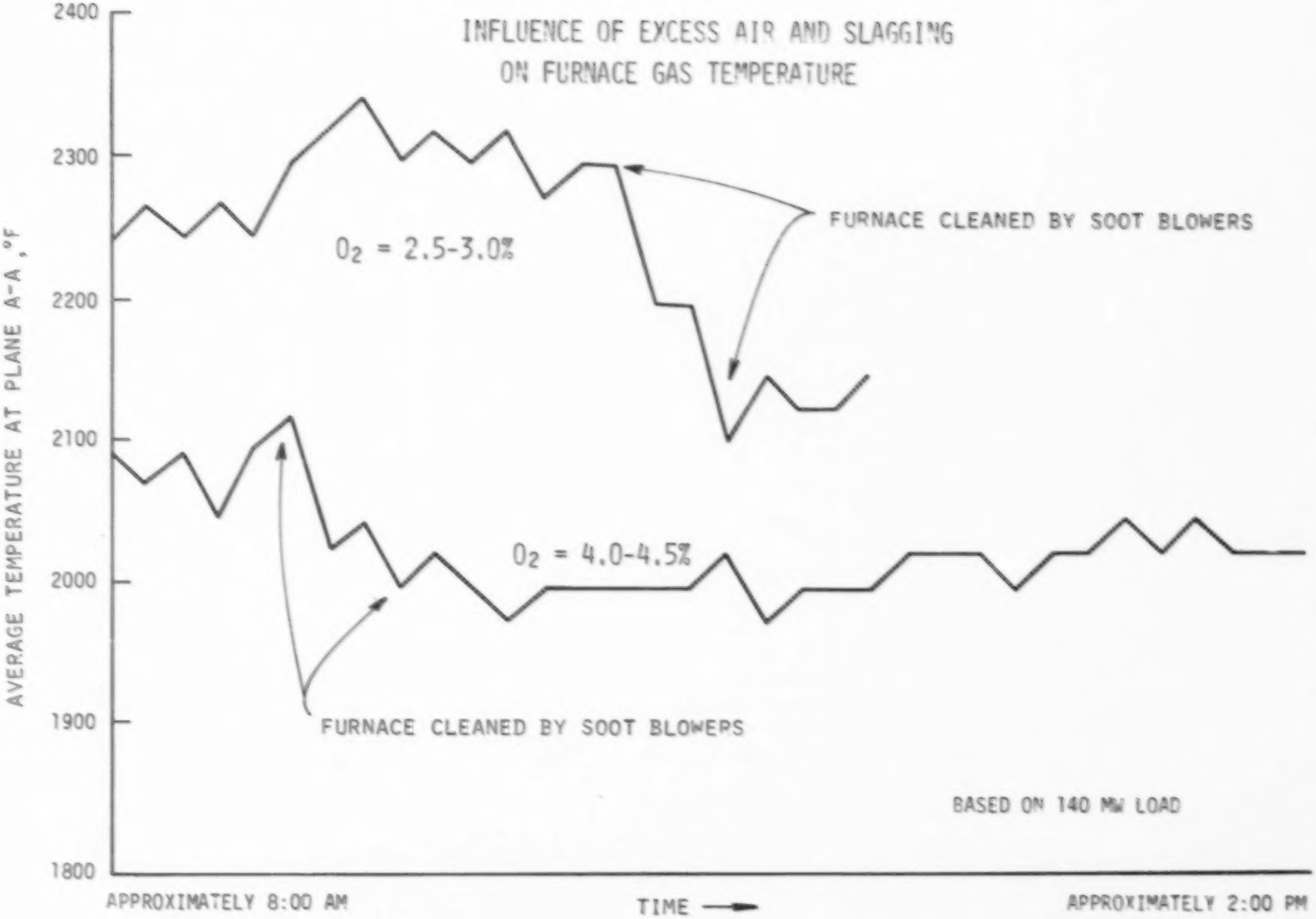
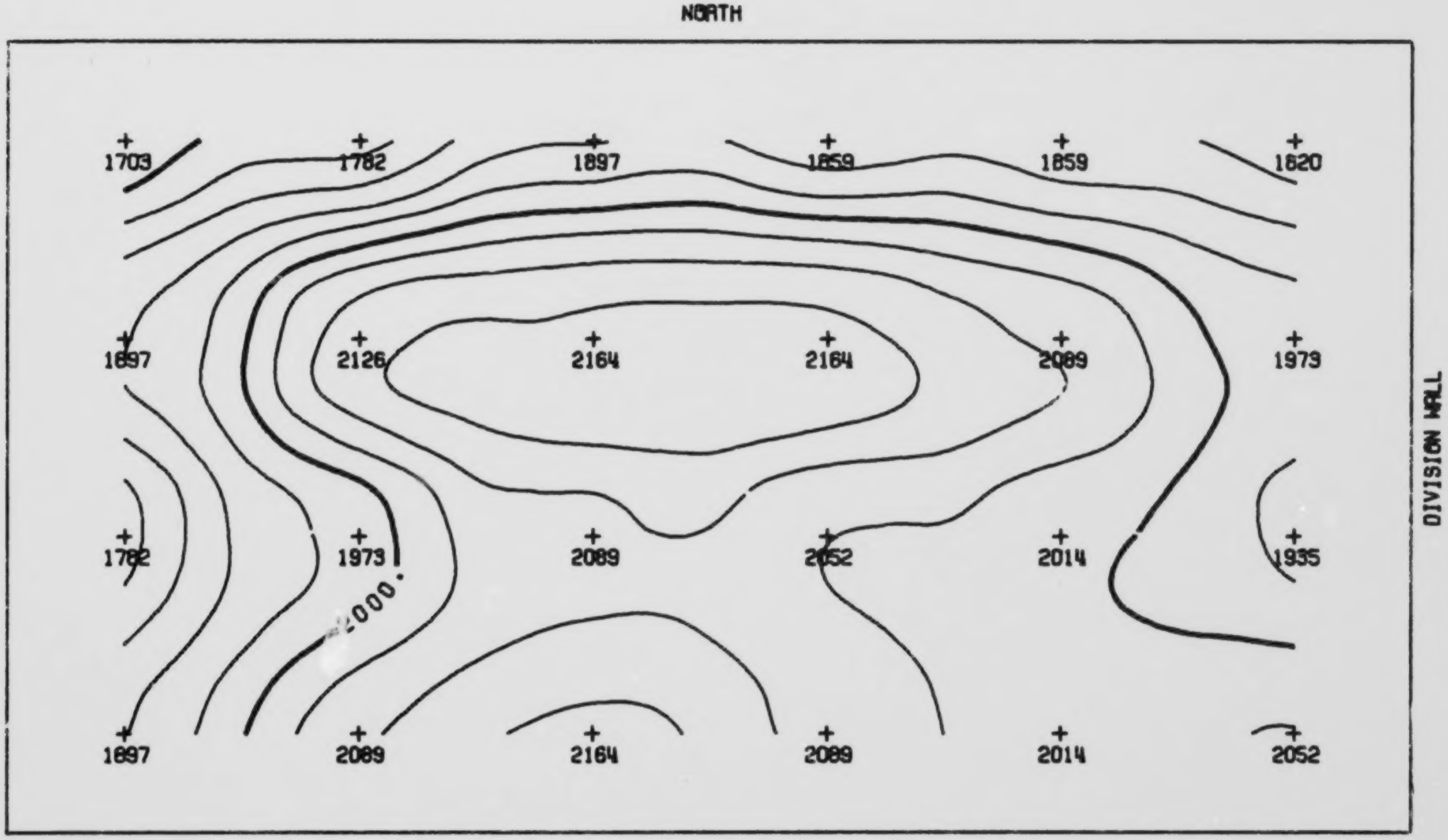


FIGURE 36

INFLUENCE OF EXCESS AIR AND SLAGGING
ON FURNACE GAS TEMPERATURE

FIGURE 37

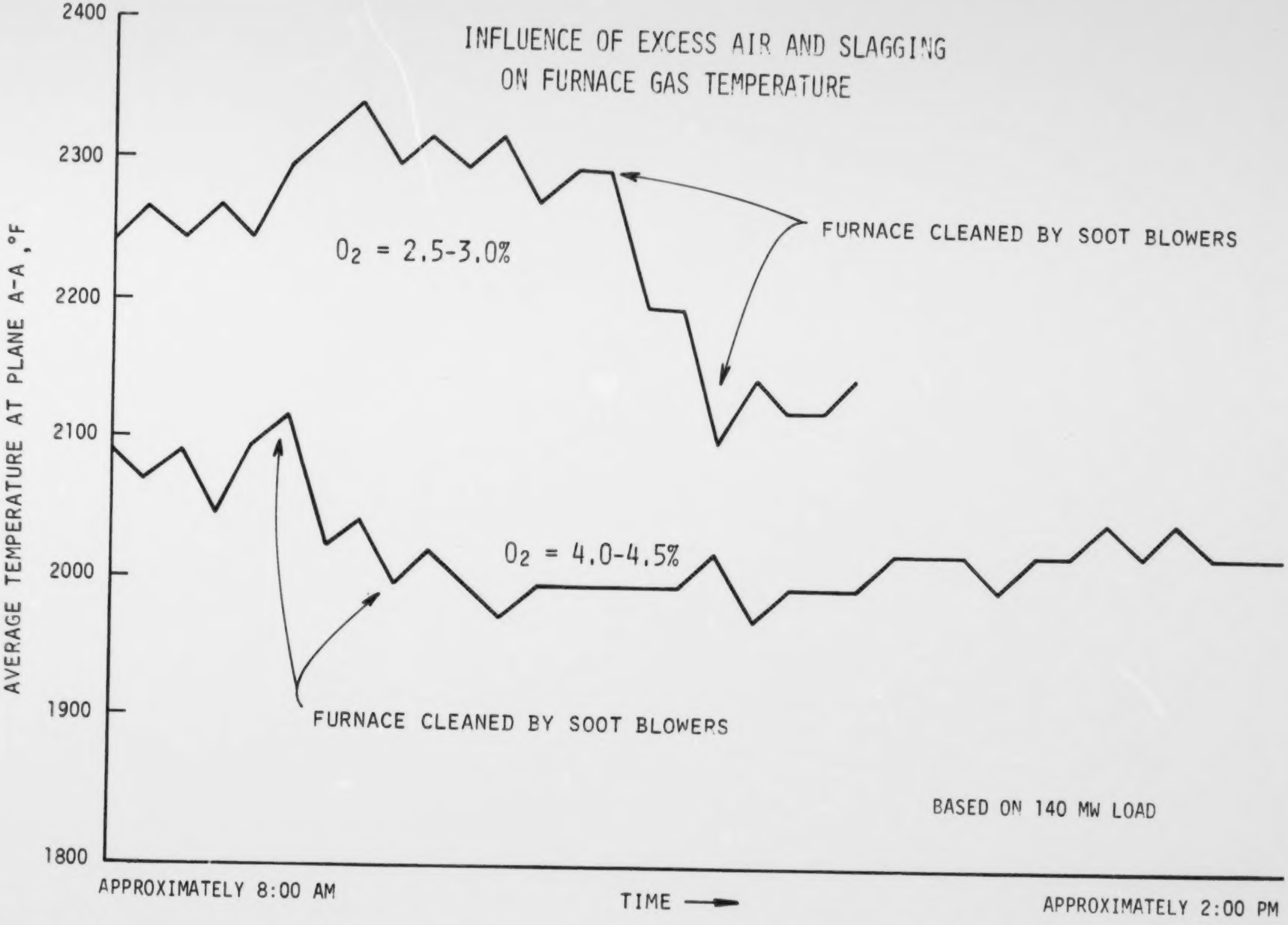


PLANE A-A WEST 11-09-70 TEST S501

ISOTHERMS - INTERVAL = 50 DEG F

Test Conditions

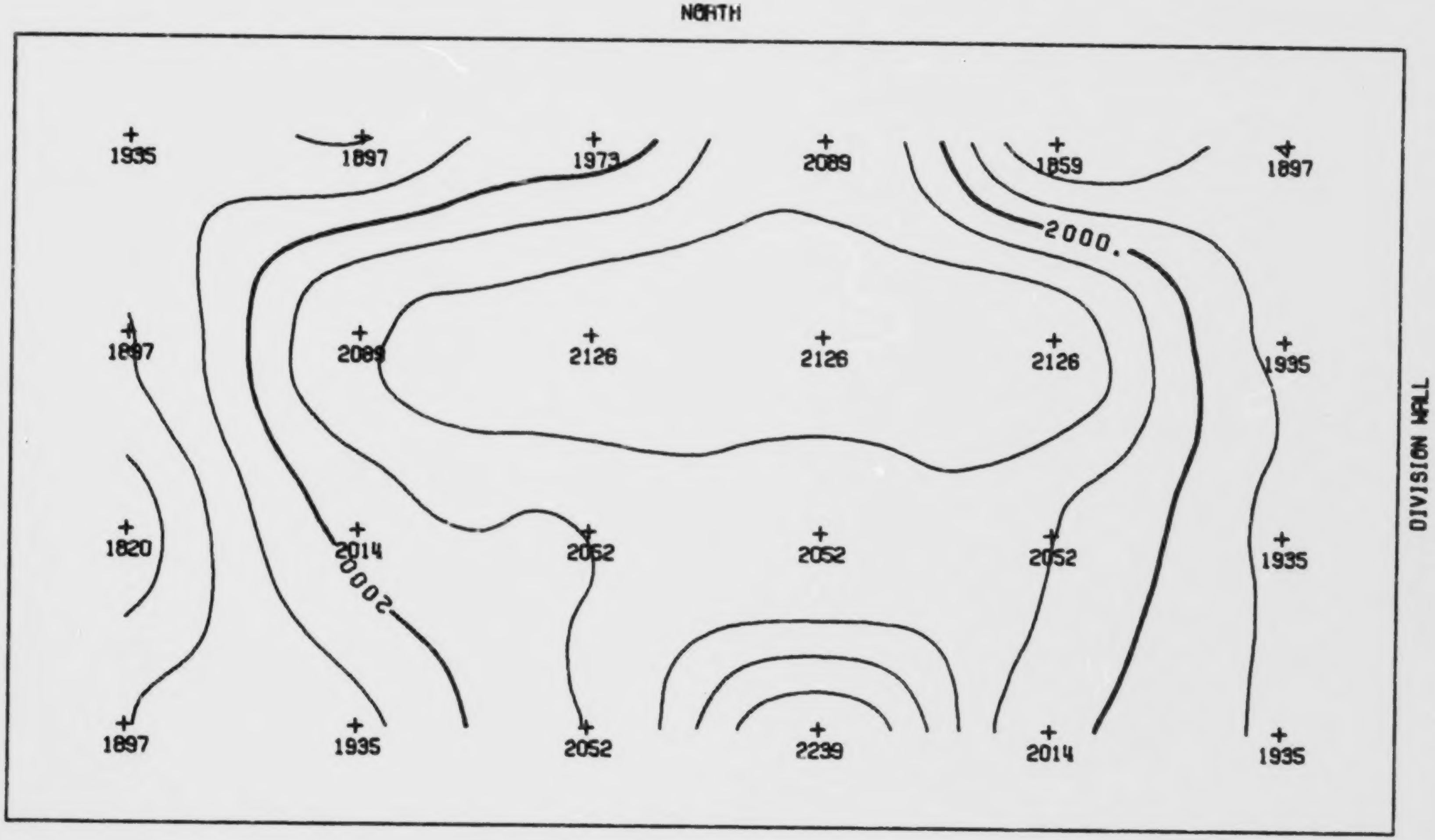
Unit load 140 MW, excess air 15%
Plane A-A avg. temp. 1978 °F
Secondary air dampers balanced



INFLUENCE OF EXCESS AIR AND SLAGGING ON FURNACE GAS TEMPERATURE

FIGURE 36

FIGURE 38



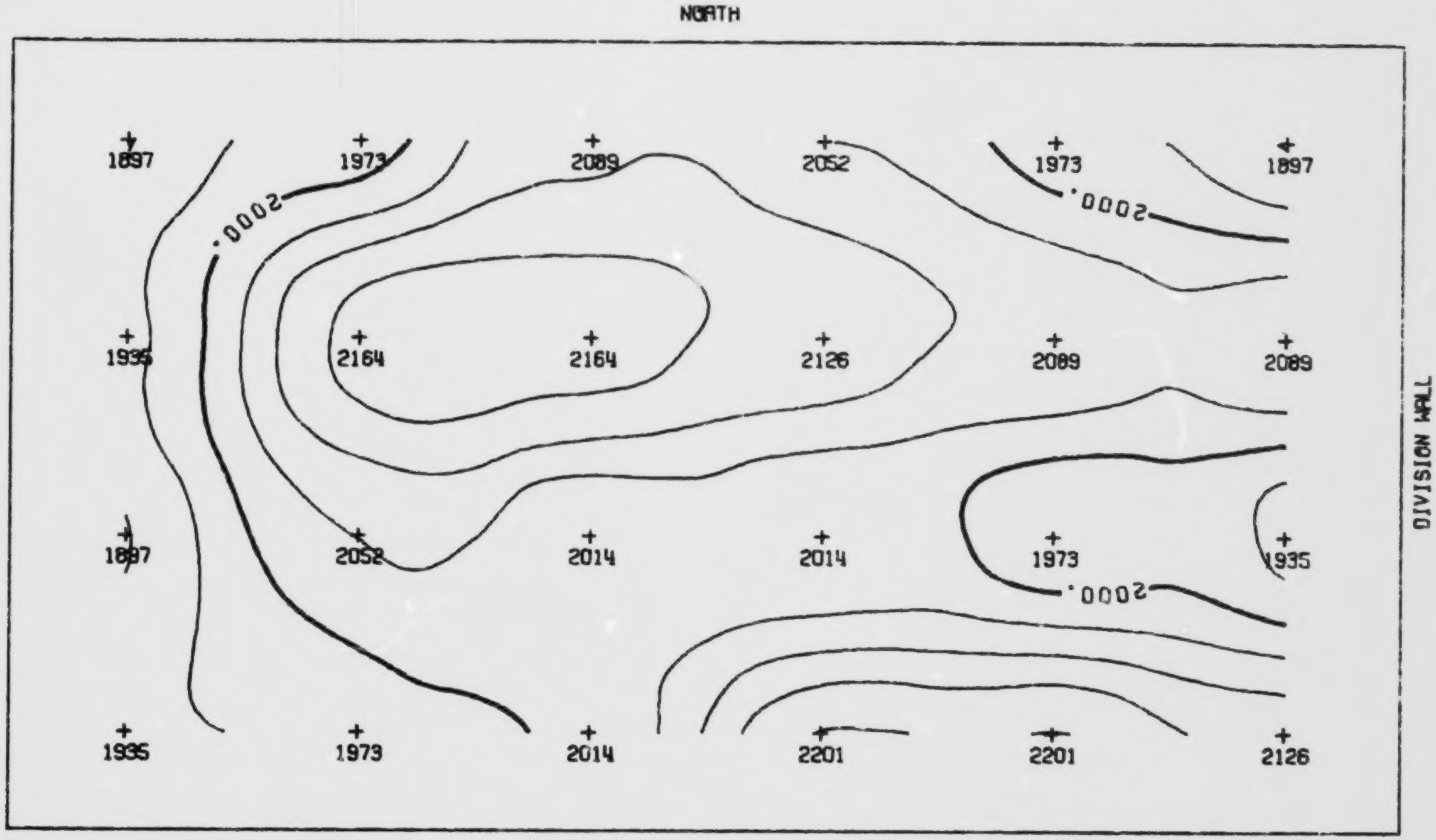
PLANE A-A WEST 11-09-70 TEST S505

ISOTHERMS - INTERVAL = 50 DEG F

Test Conditions

Unit load 140 MW, excess air 15%
Plane A-A avg. temp. 1998 °F
Secondary air dampers balanced

FIGURE 39

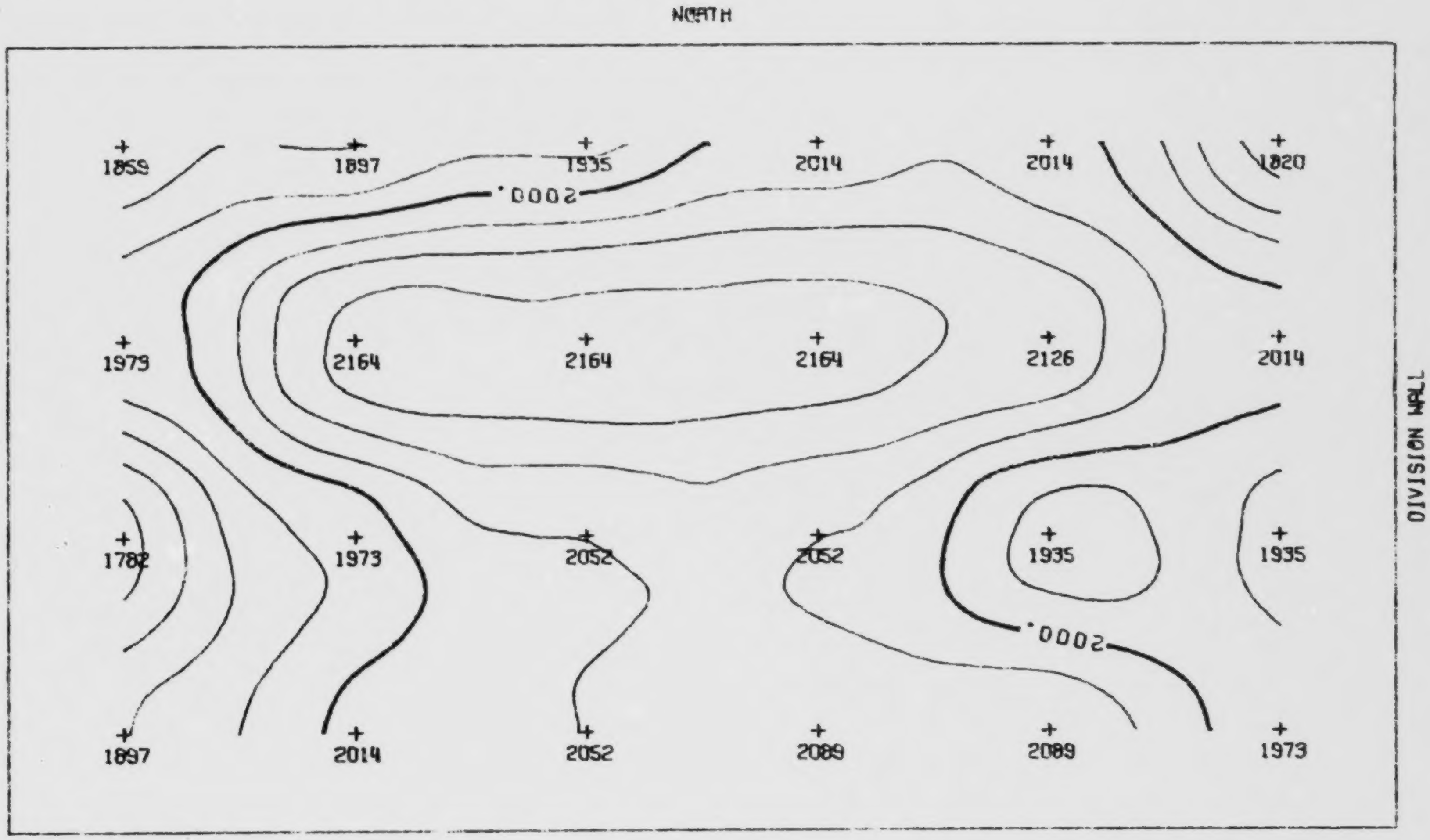


PLANE A-A WEST 11-09-70 TEST S510

ISOTHERMS - INTERVAL = 50 DEG F

Test Conditions

Unit load 140 MW, excess air 18%
Plane A-A avg. temp. 2033 °F
Secondary air dampers balanced



PLANE A-A WEST 11-09-70 TEST S515

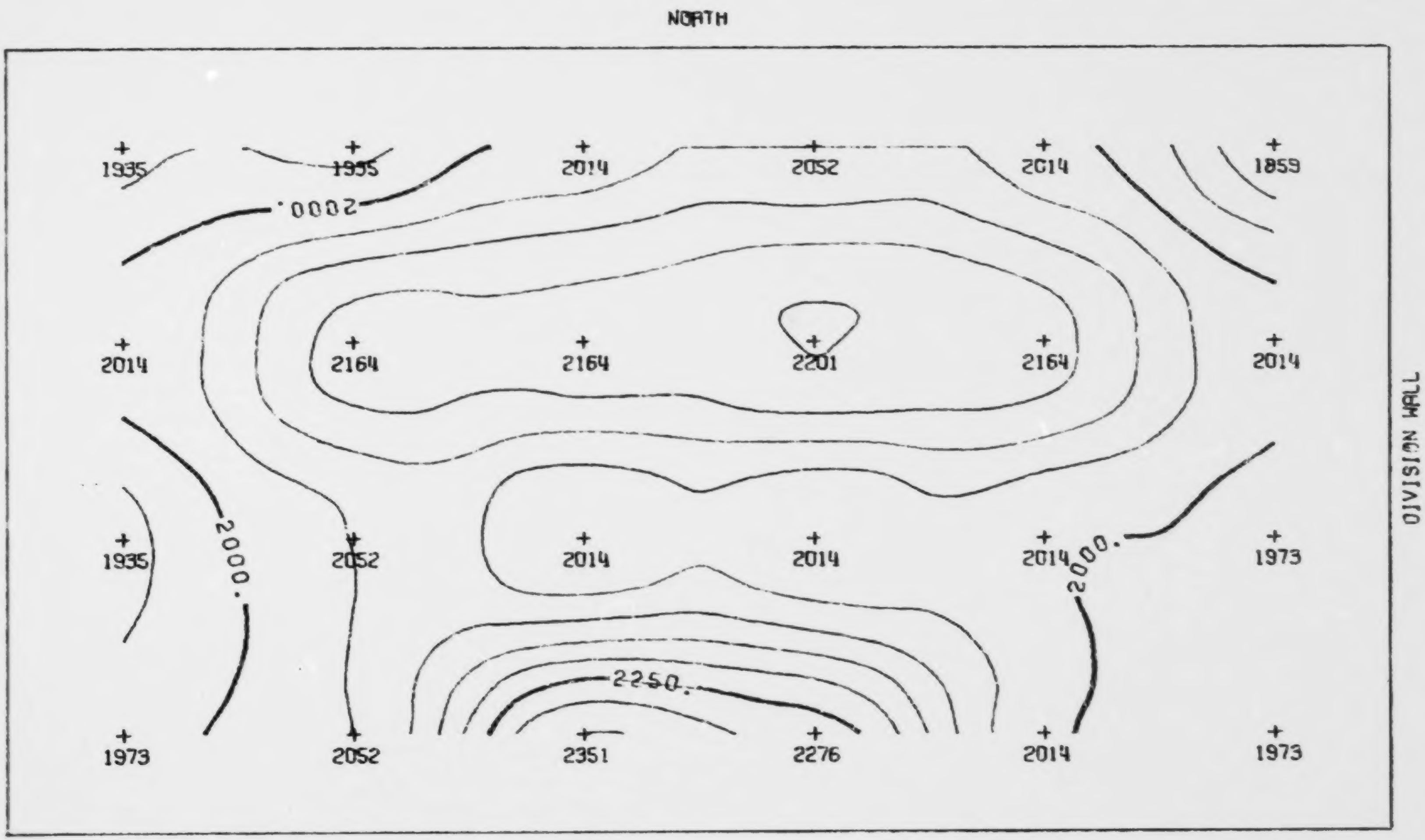
ISOTHERMS - INTERVAL = 50 DEG F

Test Conditions

Unit load 140 MW, excess air 21%
Plane A-A avg. temp. 1999 °F
Secondary air dampers balanced

FIGURE 40

FIGURE 41

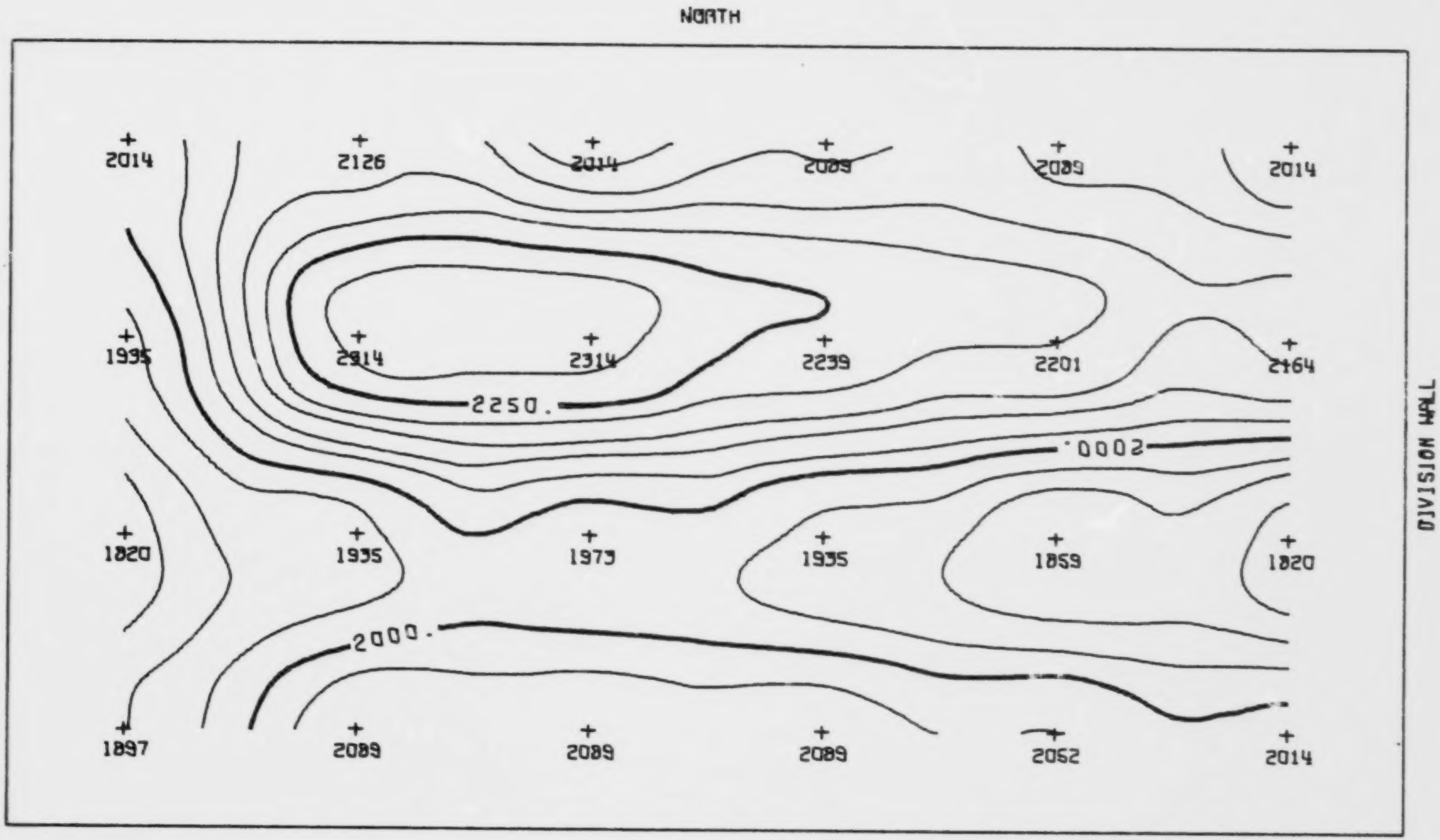


PLANE A-A WEST 11-09-70 TEST S518

ISOTHERMS - INTERVAL = 50 DEG F

Test Conditions

Unit load 140 MW, excess air 21%
Plane A-A avg. temp. 2049 °F
Secondary air dampers balanced



PLANE A-A WEST 11-16-70 TEST S501

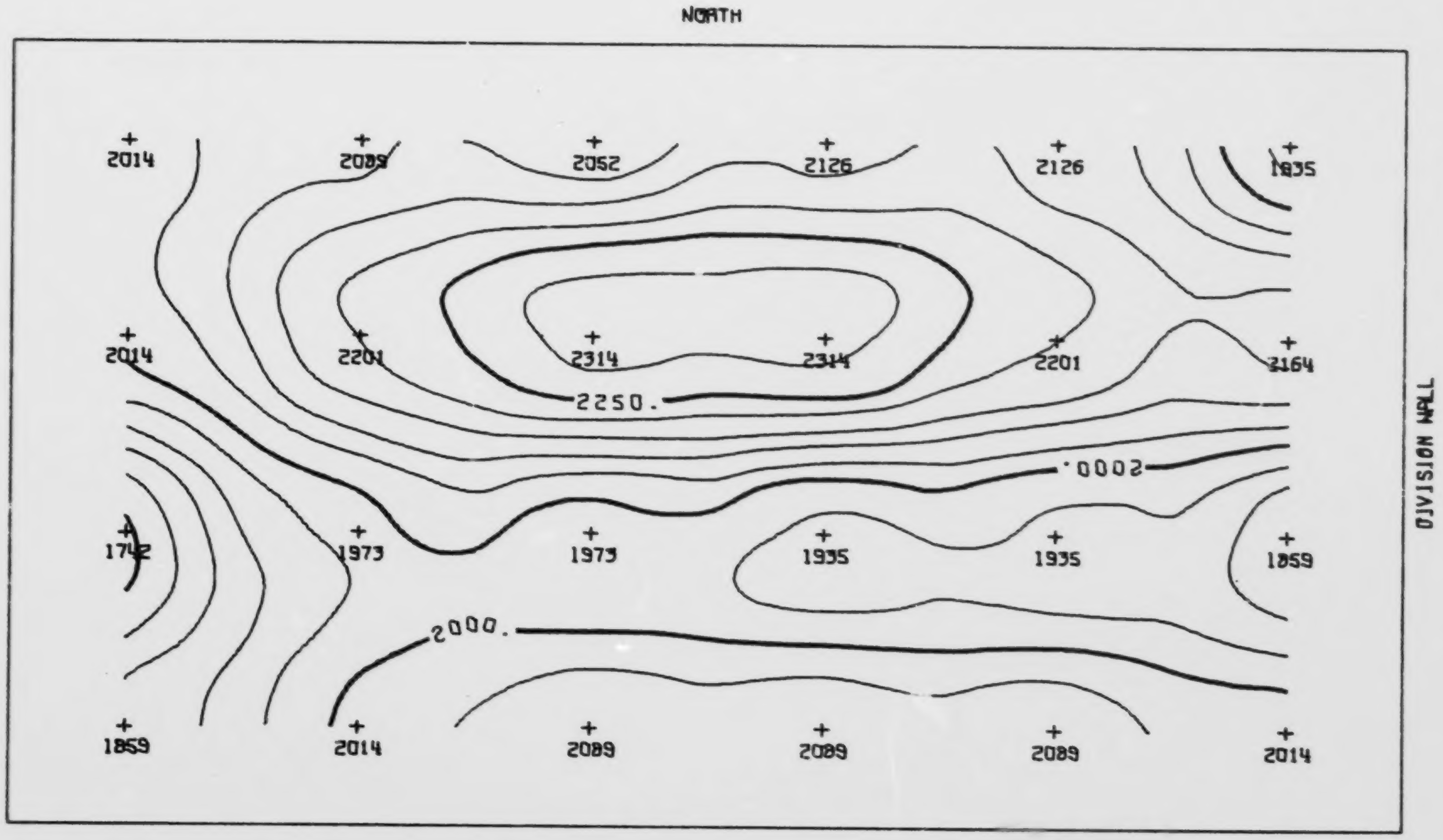
ISOTHERMS - INTERVAL = 50 DEG F

Test Conditions

Unit load 141 MW, excess air 27%
Plane A-A avg. temp. 2045 °F
Secondary air dampers unbalanced

FIGURE 42

FIGURE 43

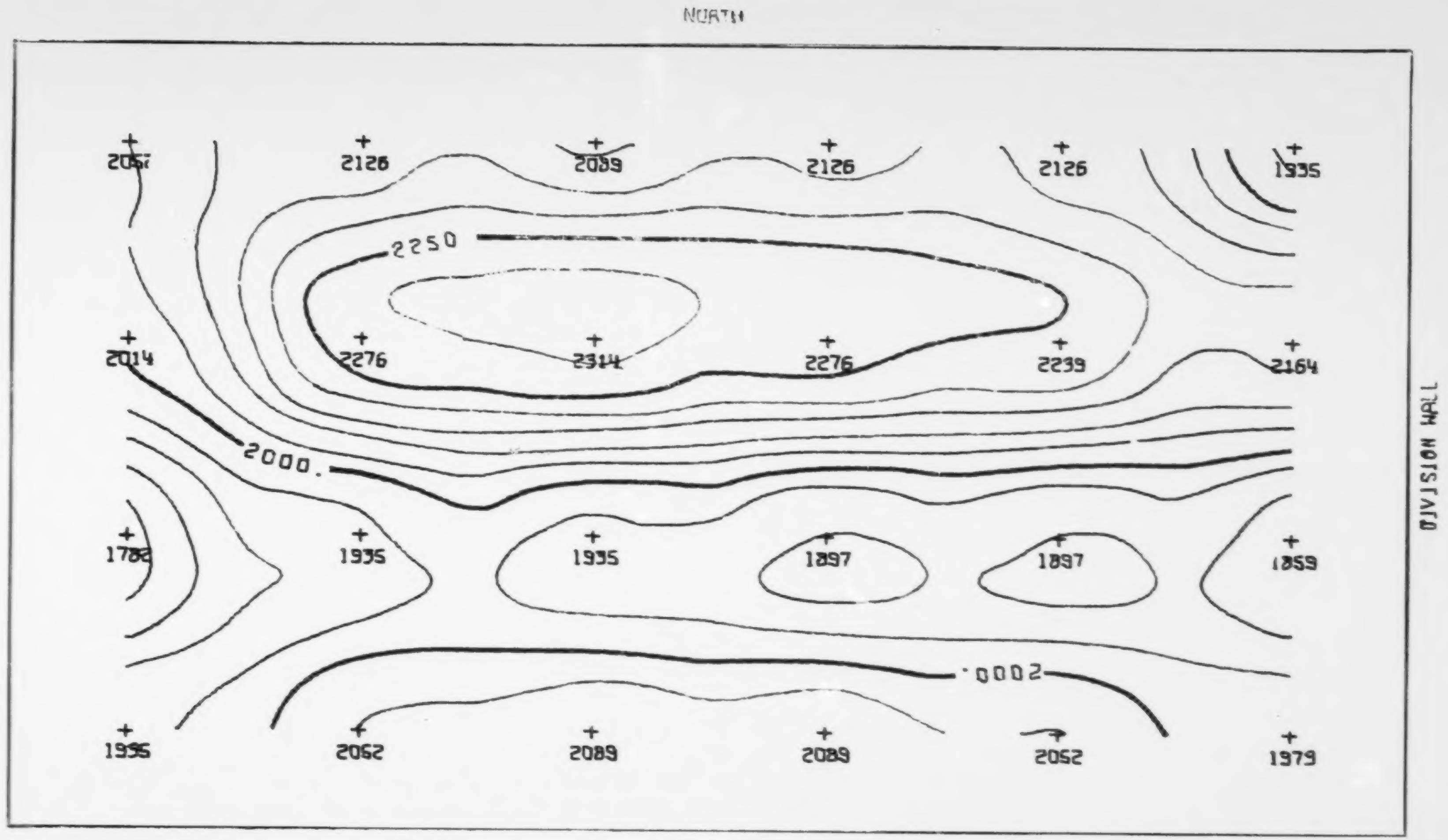


PLANE A-A WEST 11-16-70 TEST S505

ISOTHERMS - INTERVAL = 50 DEG F

Test Conditions

Unit load 141 MW, excess air 27%
Plane A-A avg. temp. 2047 °F
Secondary air dampers unbalanced



PLANE A-A WEST 11-16-70 TEST S510

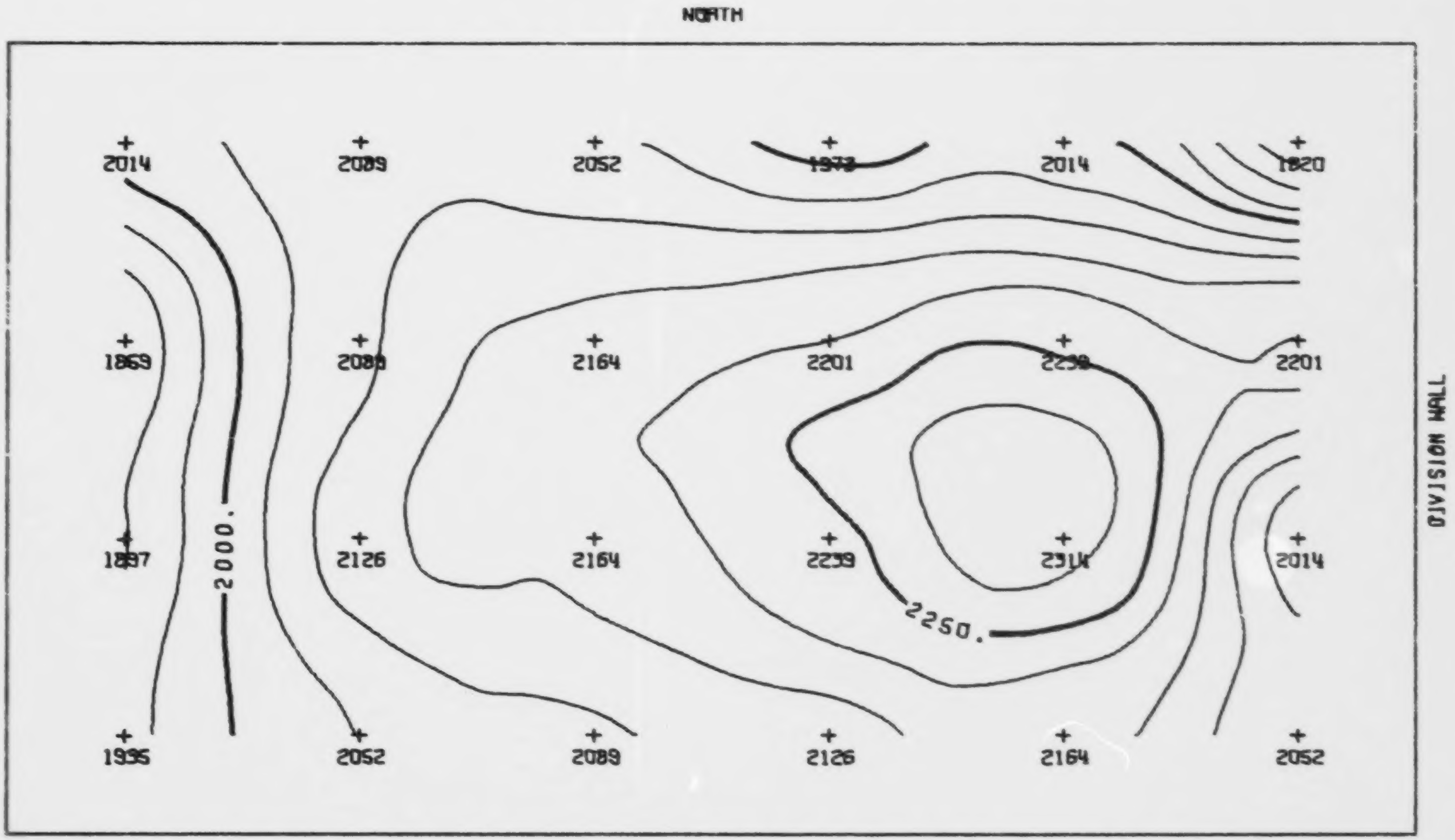
ISOTHERMS - INTERVAL = 50 DEG F

Test Contidions

Unit load 141 MW, excess air 27%
Plane A-A avg. temp. 2051 °F
Secondary air dampers unbalanced

FIGURE 44

FIGURE 45



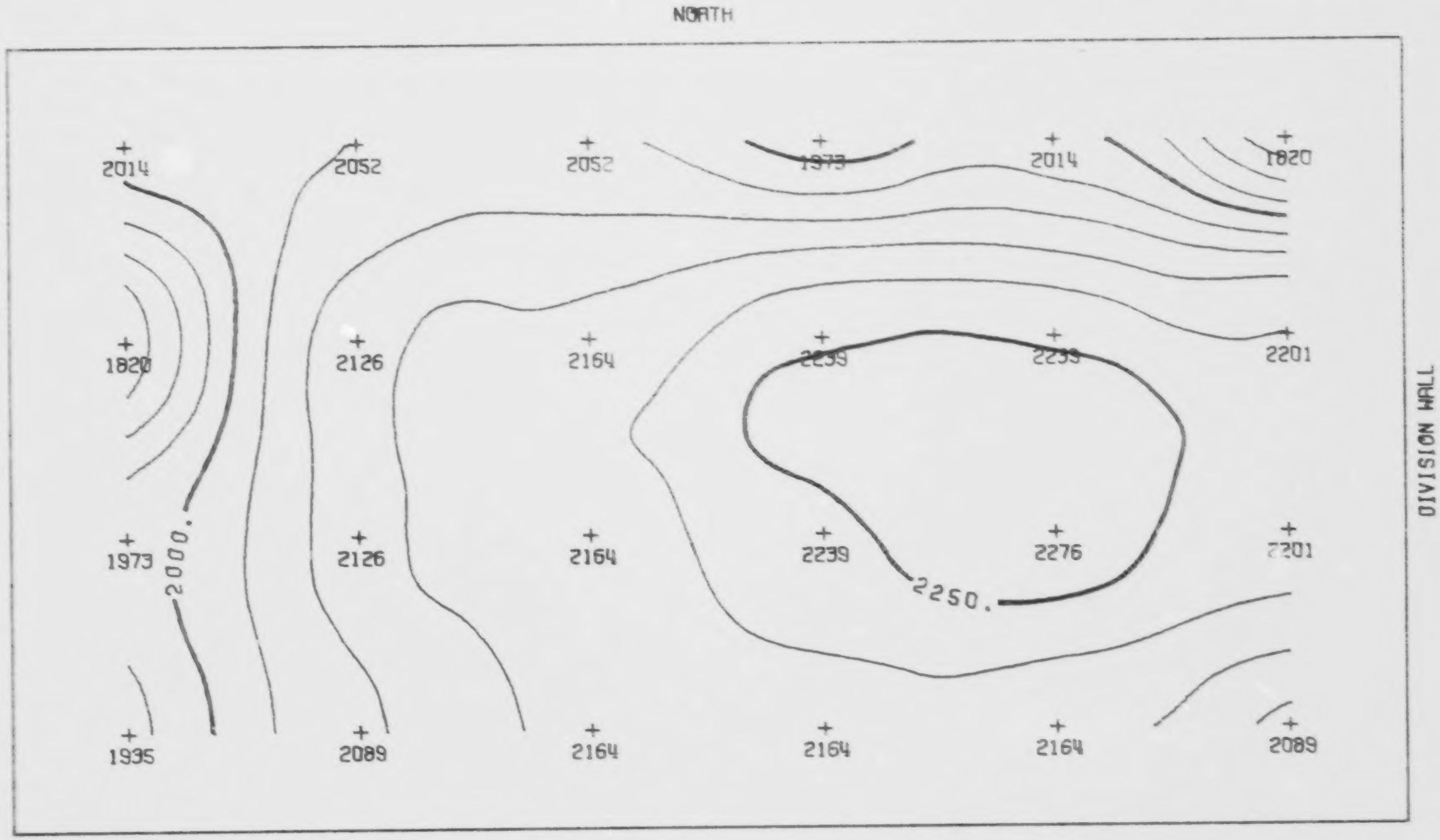
PLANE A-A WEST 11-16-70 TEST S514

ISOTHERMS - INTERVAL = 50 DEG F

Test Conditions

Unit load 141 MW, excess air 27%
Plane A-A avg. temp. 2079 °F
Secondary air dampers unbalanced

FIGURE 46



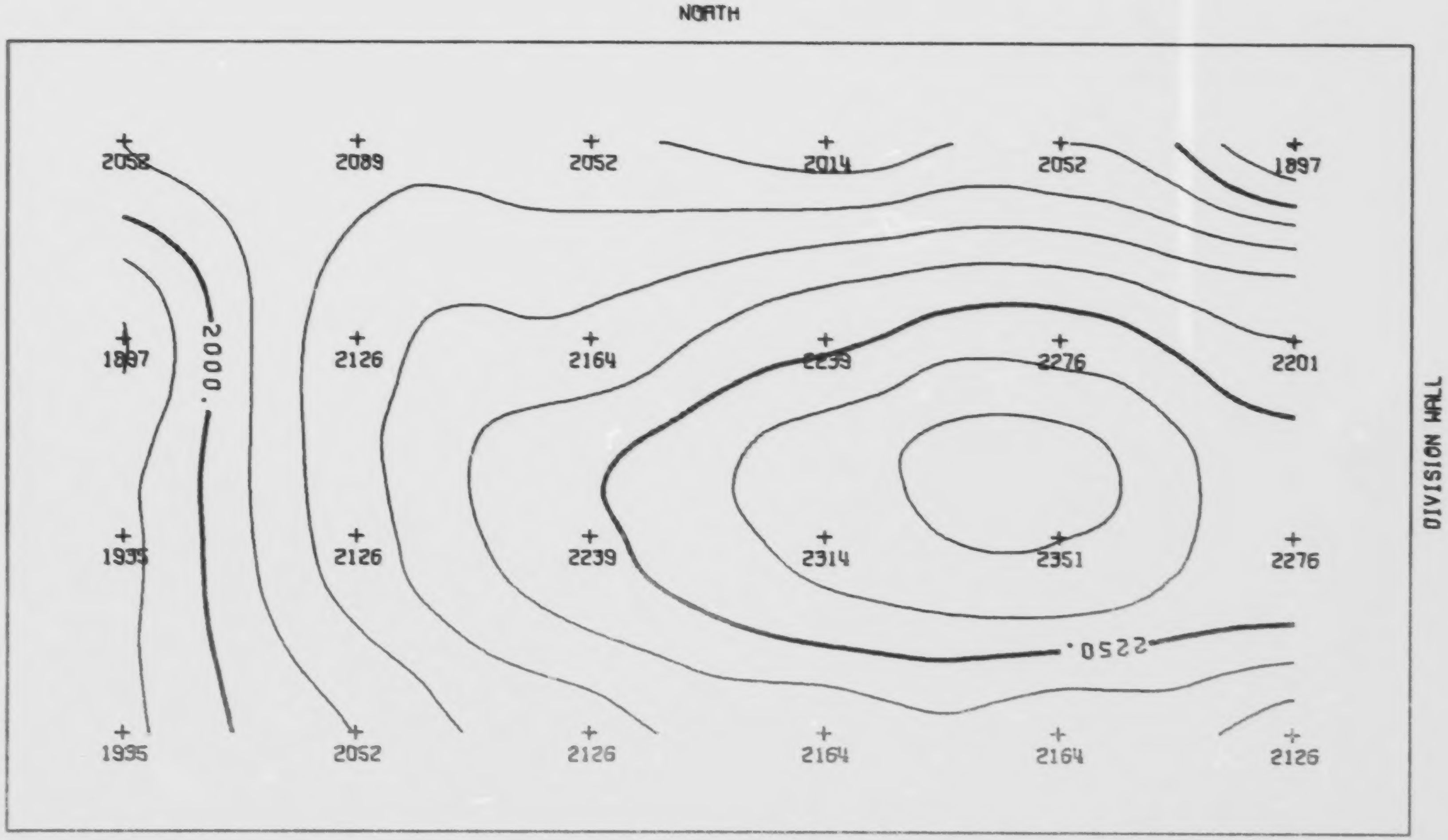
PLANE A-A WEST 11-16-70 TEST S520

ISOTHERMS - INTERVAL = 50 DEG F

Test Conditions

Unit load 141 MW, excess air 27%
Plane A-A avg. temp. 2096 °F
Secondary air dampers unbalanced

FIGURE 47



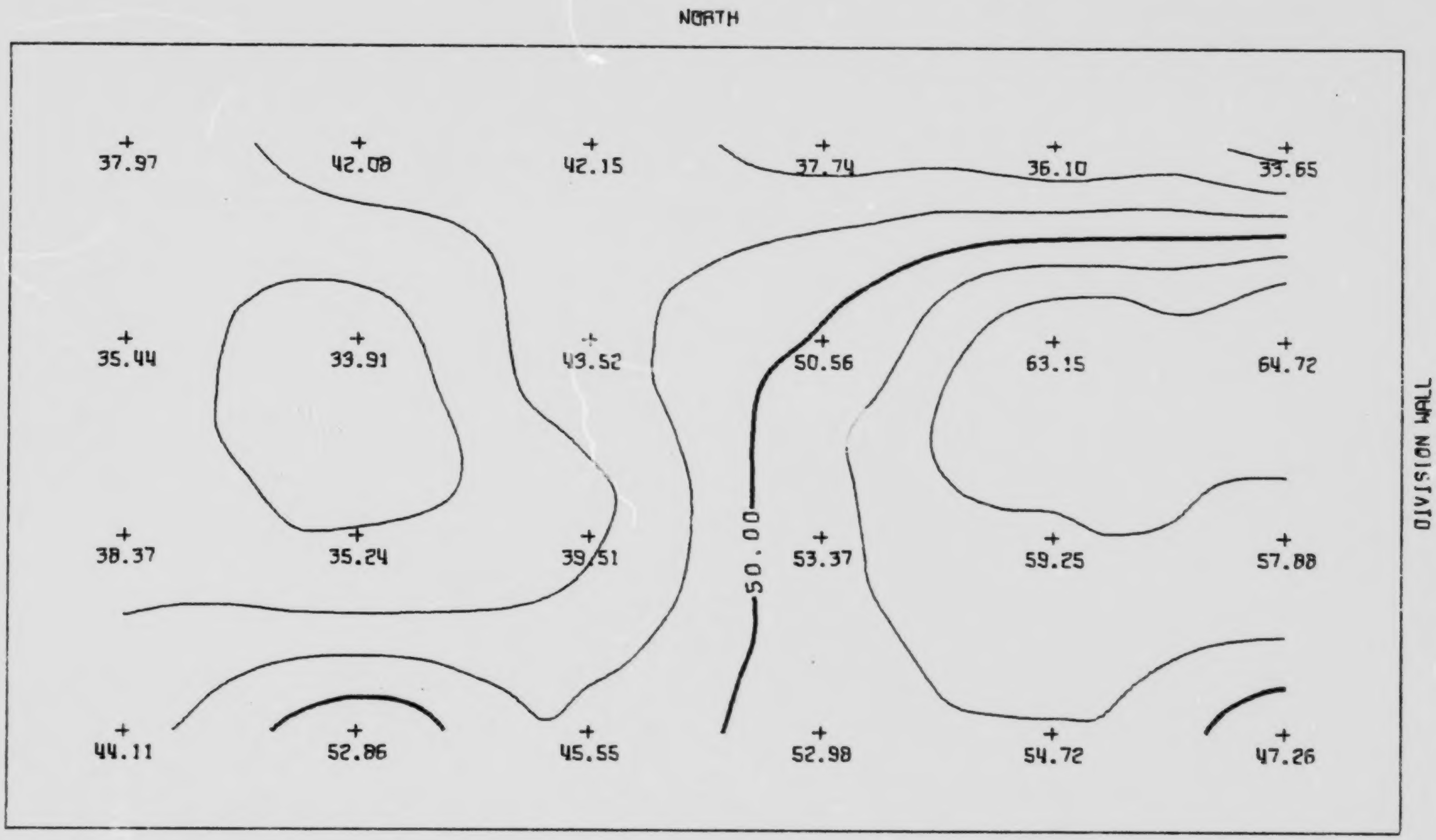
PLANE A-A WEST 11-16-70 TEST S522

ISOTHERMS - INTERVAL = 50 DEG F

Test Conditions

Unit load 141 MW, excess air 27%
Plane A-A avg. temp. 2119 °F
Secondary air dampers unbalanced

FIGURE 48



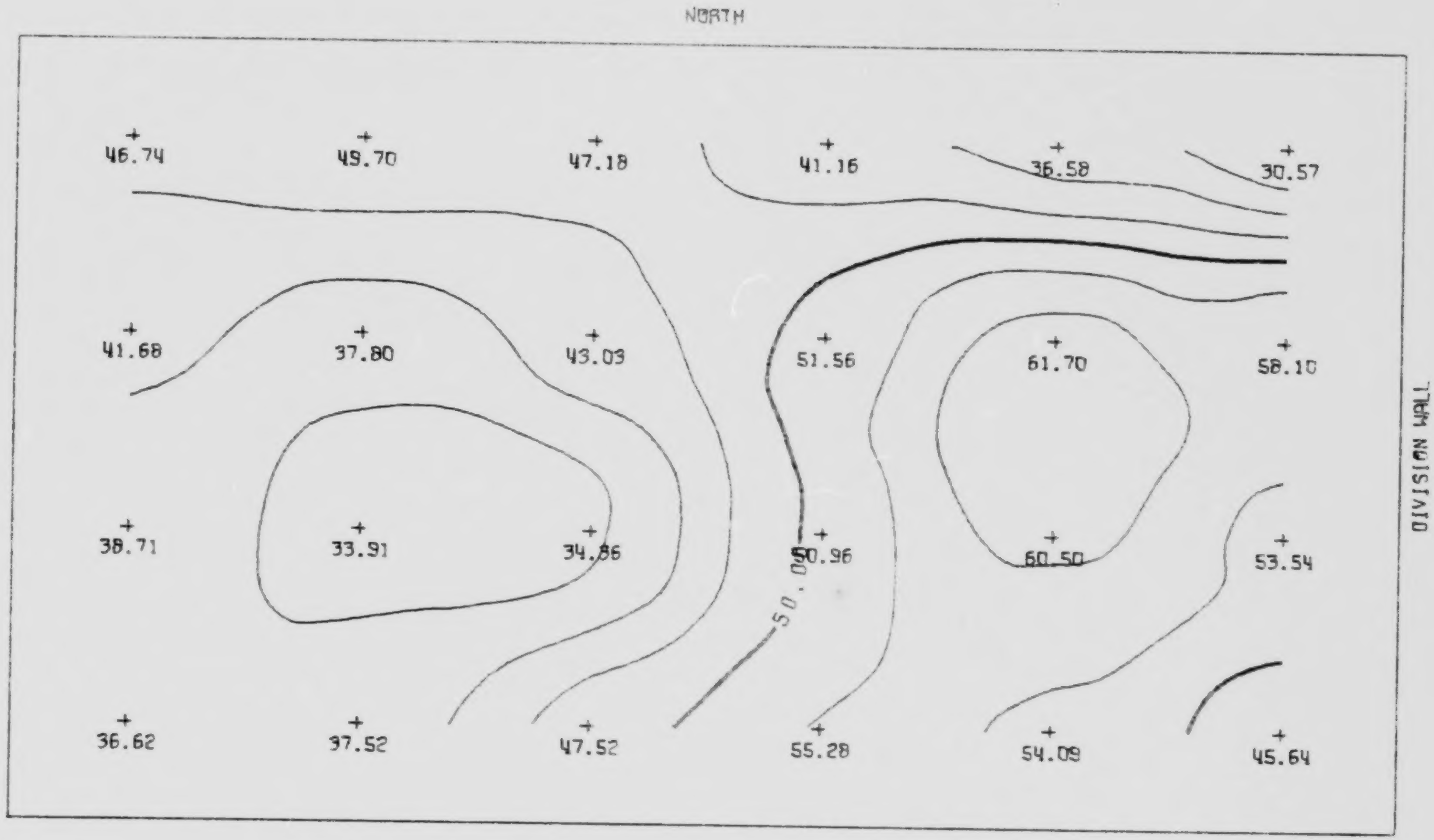
PLANE A-A WEST 12-3-70 TEST S601

CAO IN DUST SAMPLE - % INT = 5

Test Conditions

Unit load 143 MW, excess air 24%
Plane A-A avg. CaO in dust 45.9%
Secondary air dampers balanced
Injection at lower rear @ 0°
Fredonia limestone @ 1.74 stoich.

FIGURE 49



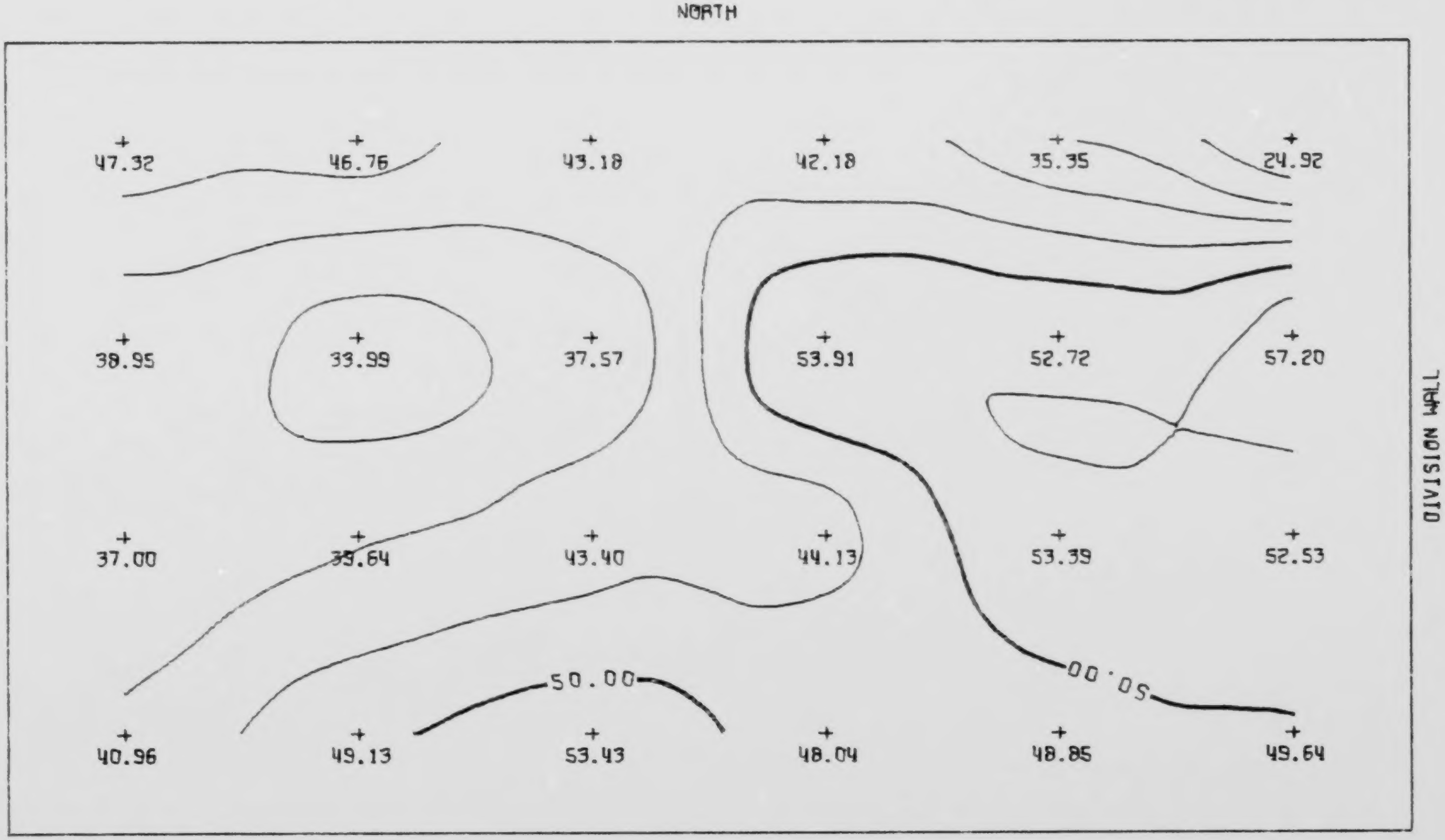
PLANE A-A WEST 12-3-70 TEST S602

CAO IN DUST SAMPLE - % INT = 5

Test Conditions

Unit load 143 MW, excess air 24%
Plane A-A avg. CaO in dust 45.60%
Secondary air dampers balanced
Injection at lower rear @ 0°
Fredonia limestone @ 1.74 stoich.

FIGURE 50



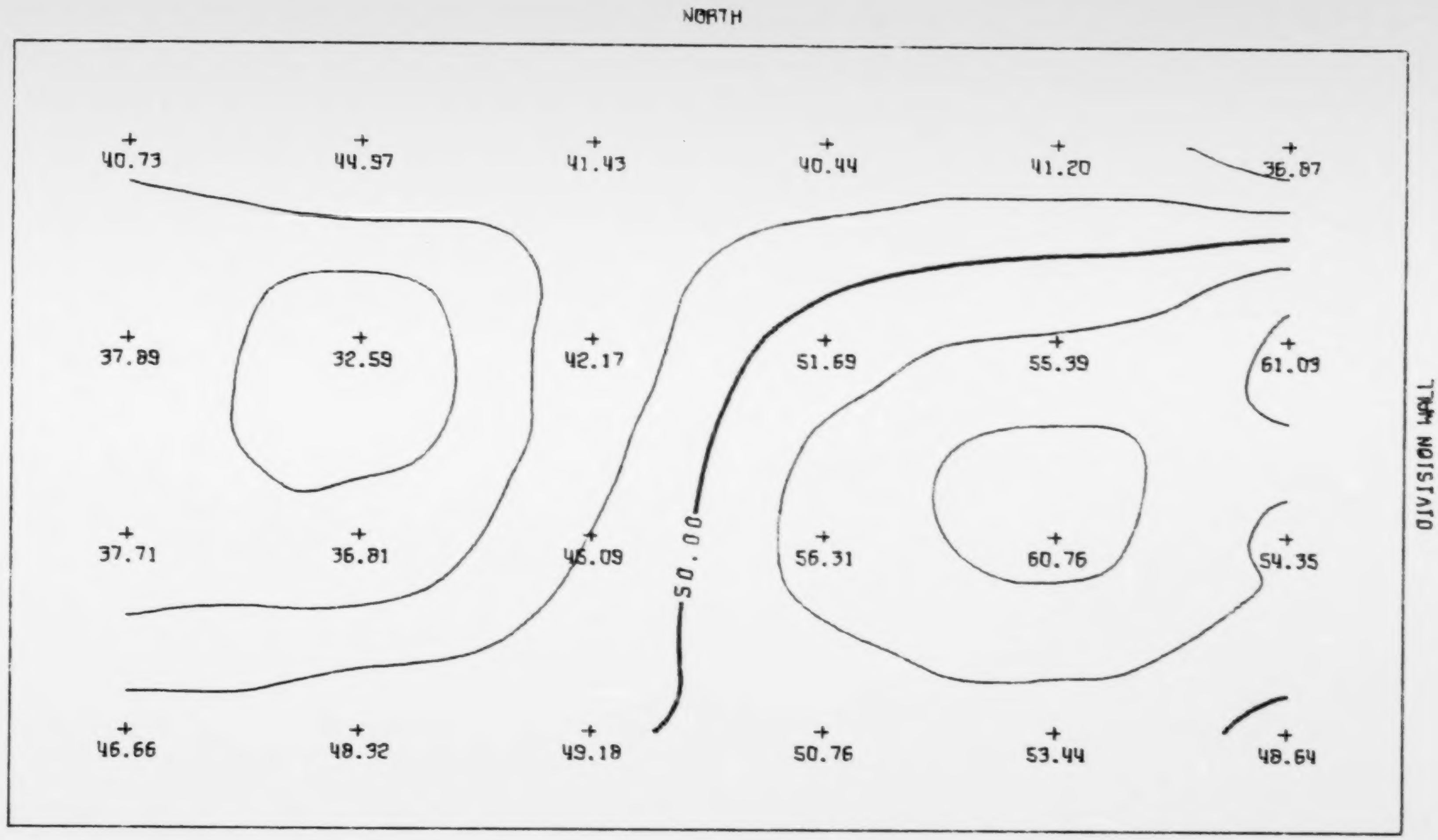
PLANE A-A WEST 12-3-70 TEST S603

CAO IN DUST SAMPLE - % INT = 5

Test Conditions

Unit load 143 MW, excess air 24%
Plane A-A avg. CaO in dust 44.76%
Secondary air dampers balanced
Injection at lower rear @ 0°
Fredonia limestone @ 1.74 stoich.

FIGURE 51



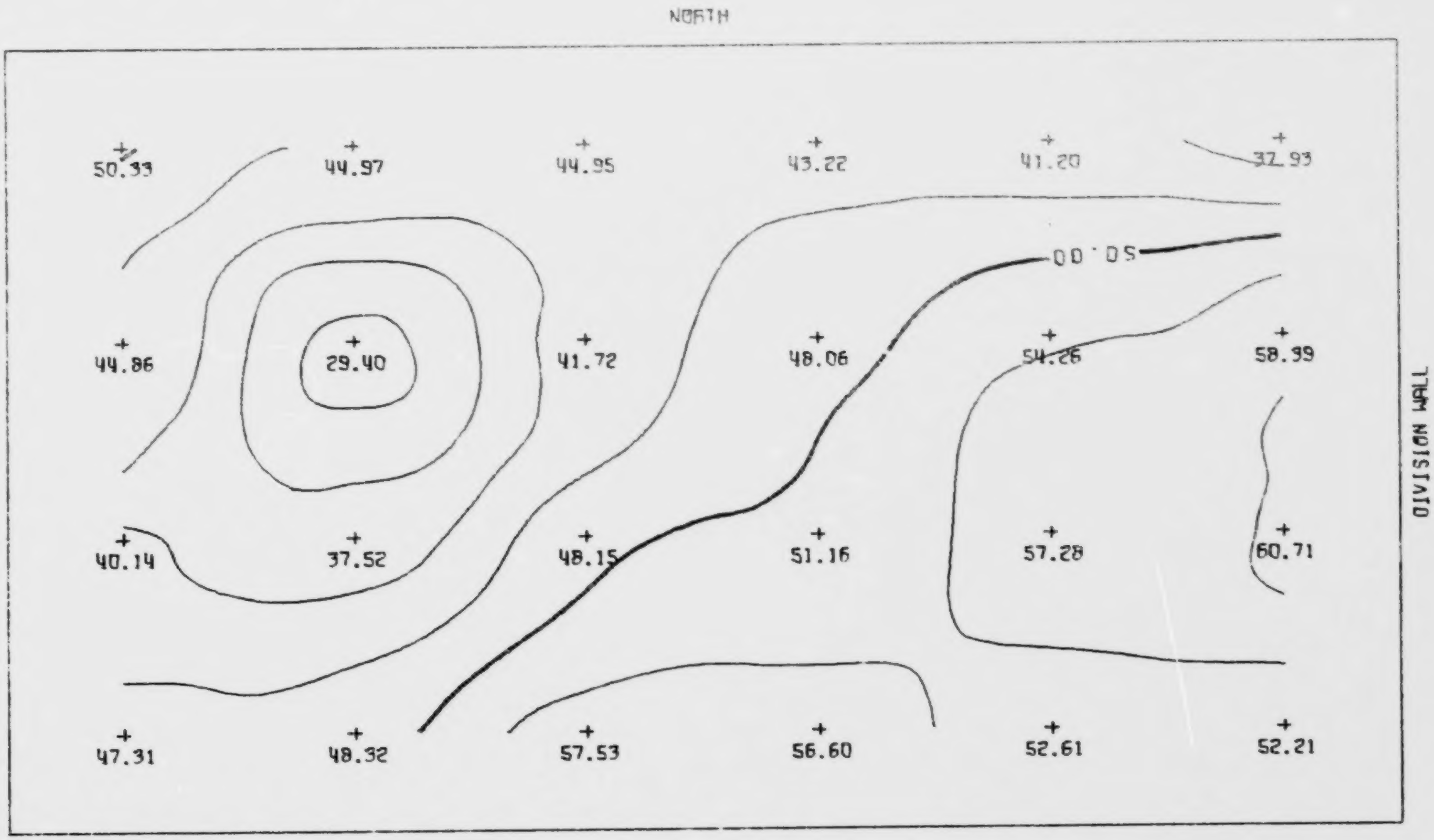
PLANE A-A WEST 12-3-70 TEST S604

CAO IN DUST SAMPLE - % INT = 5

Test Conditions

Unit load 143 MW, excess air 24%
Plane A-A avg. CaO in dust 46.43%
Secondary air dampers balanced
Injection at lower rear @ 0°
Fredonia limestone @ 1.74 stoich.

FIGURE 52



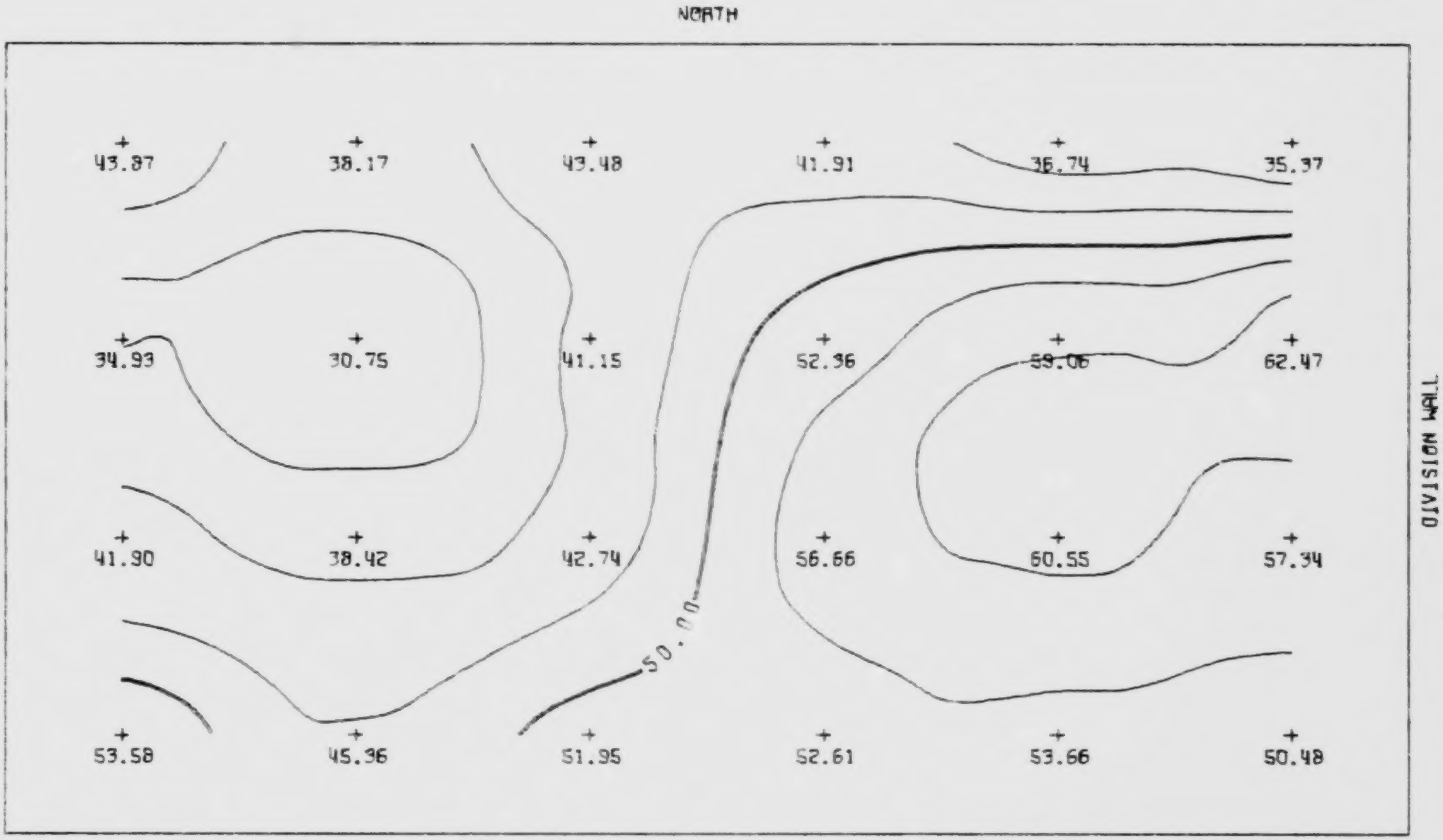
PLANE A-A WEST 12-3-70 TEST S605

CAO IN DUST SAMPLE - % INT = 5

Test Conditions

Unit load 143 MW, excess air 24%
Plane A-A avg. CaO in dust 47.87%
Secondary air dampers balanced
Injection at lower rear @ 0°
Fredonia limestone @ 1.74 stoich.

FIGURE 53



PLANE A-A WEST 12-3-70 TEST S606

CAO IN DUST SAMPLE - % INT = 5

Test Conditions

Unit load 143 MW, excess air 24%
Plane A-A avg. CaO in dust 46.90%
Secondary air dampers balanced
Injection at lower rear @ 0°
Fredonia limestone @ 1.74 stoich

e. Instantaneous Dust Distribution

The hypothesis was advanced by Thomas[20] that large "bubbles" of flue gas, perhaps 10 feet in diameter, might be passing through the furnace without receiving the proper ratio of injected limestone. The SO_2 within these "bubbles" would not be in contact with CaO and, therefore, would not be converted to $CaSO_4$. It was necessary to first try to detect if such bubbles existed and then to attempt measurement of dust concentration by some in-situ technique. Two possible methods selected for study were (1) laser holography and (2) tape dust sampler.

Extensive research carried out by TRW Systems, Inc., demonstrated that holograms of furnace combustion can detect, physically locate and dimension regions of high dust concentration across the 24-foot furnace width where there are directly opposing ports. In the region of interest (plane A-A), the absence of opposing ports required investigation of laser back scatter or side scatter. Because more development time would be required than was available in this phase of testing the additional effort was not expended. More complete information on support activity is provided in appendix E.

Development effort was also applied by TVA to use a tape dust sampler fixed to the end of a water-cooled probe. Aspirated flue gas was passed into the sampler where dust particles were deposited continuously on moving paper tape for subsequent analysis. This technique gave some promise of determining lime concentration variations with time but neither this method nor the holograms identified the existence of "bubbles." It was decided to discontinue the study. Further information on results with this sampler are also given in appendix E.

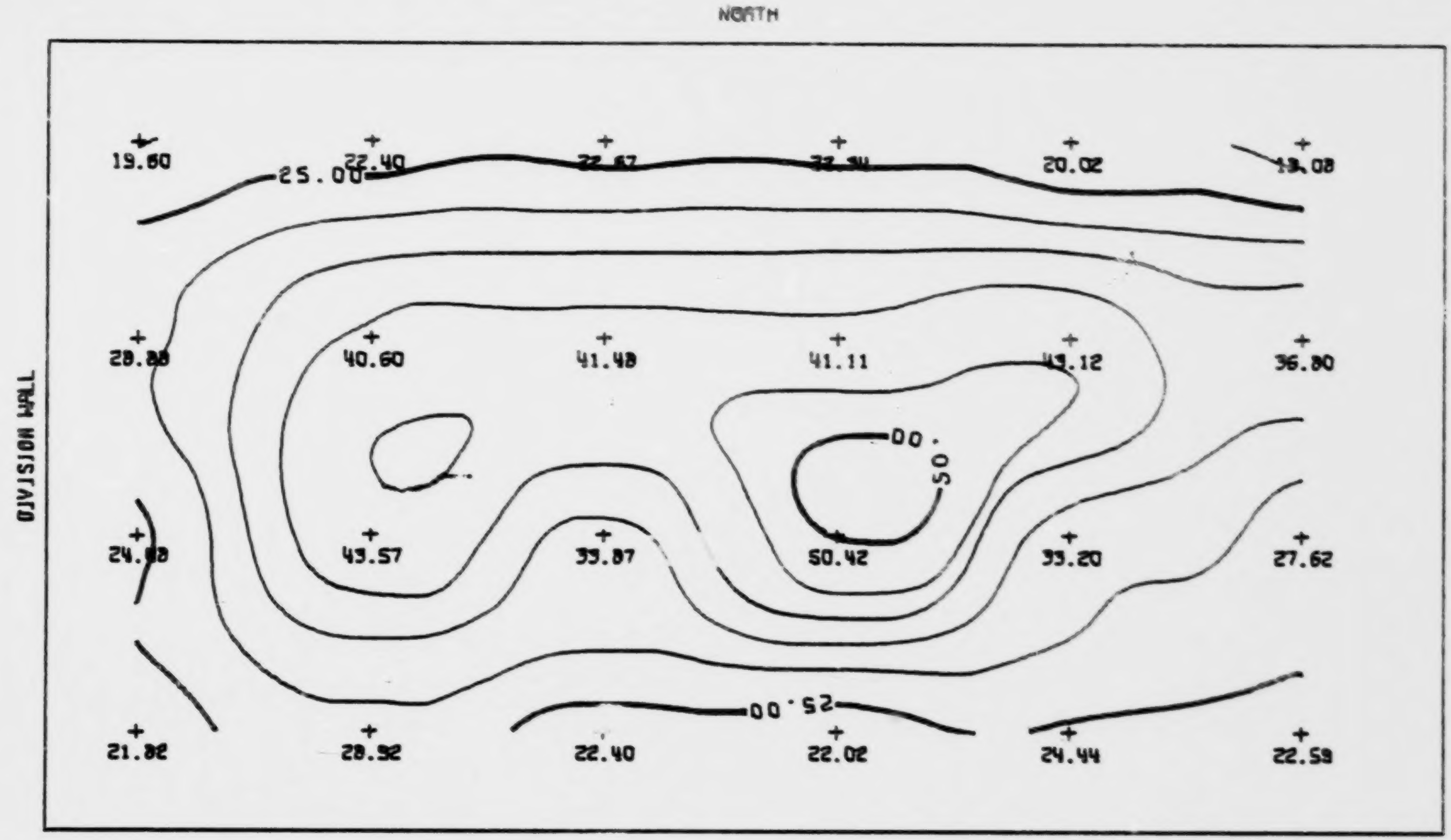
The net result of these efforts was to extend applicability of laser holography to much larger distances than had previously been accomplished in high temperature gas. Likewise, tape sampling might have verified the "bubble" phenomenon but much more effort and interpretations would have been required. If they do exist, bubbles could contribute to poor SO_2 removal by limestone injection. (Reaction chemistry models by different investigators and the nature of particle—fluid interactions on the reaction were also covered by Thomas[21].)

f. Influence of Injection Location, Angle, and Velocity on Dust Distribution

The effect on plane A-A dust distribution while injecting limestone, successively, at upper rear, lower rear, and front is shown in figures 54, 55, and 56. From these three profiles (the upper rear and front being almost identical) it is clear that furnace turbulence rather than injection elevation controls distribution. The profiles obtained from the west furnace were similar to these and lead to the same conclusion.

Front injection nozzles were structurally limited to 0° whereas upper and lower rear were variable (i.e., -45°, 0°, +45°). Only the +45° angle significantly affected dust distribution because limestone appeared to flow up the rear wall of the furnace and did not penetrate the main gas stream. Distribution for injection at -45° and 0° was similar but more deadburning of lime occurred when injecting at -45°. A very limited number of tests were conducted with simultaneous front and upper rear injection but results showed that dust distribution was not significantly affected. Figure 57 shows the CaO pattern on the west side of plane A-A during one test.

FIGURE 54



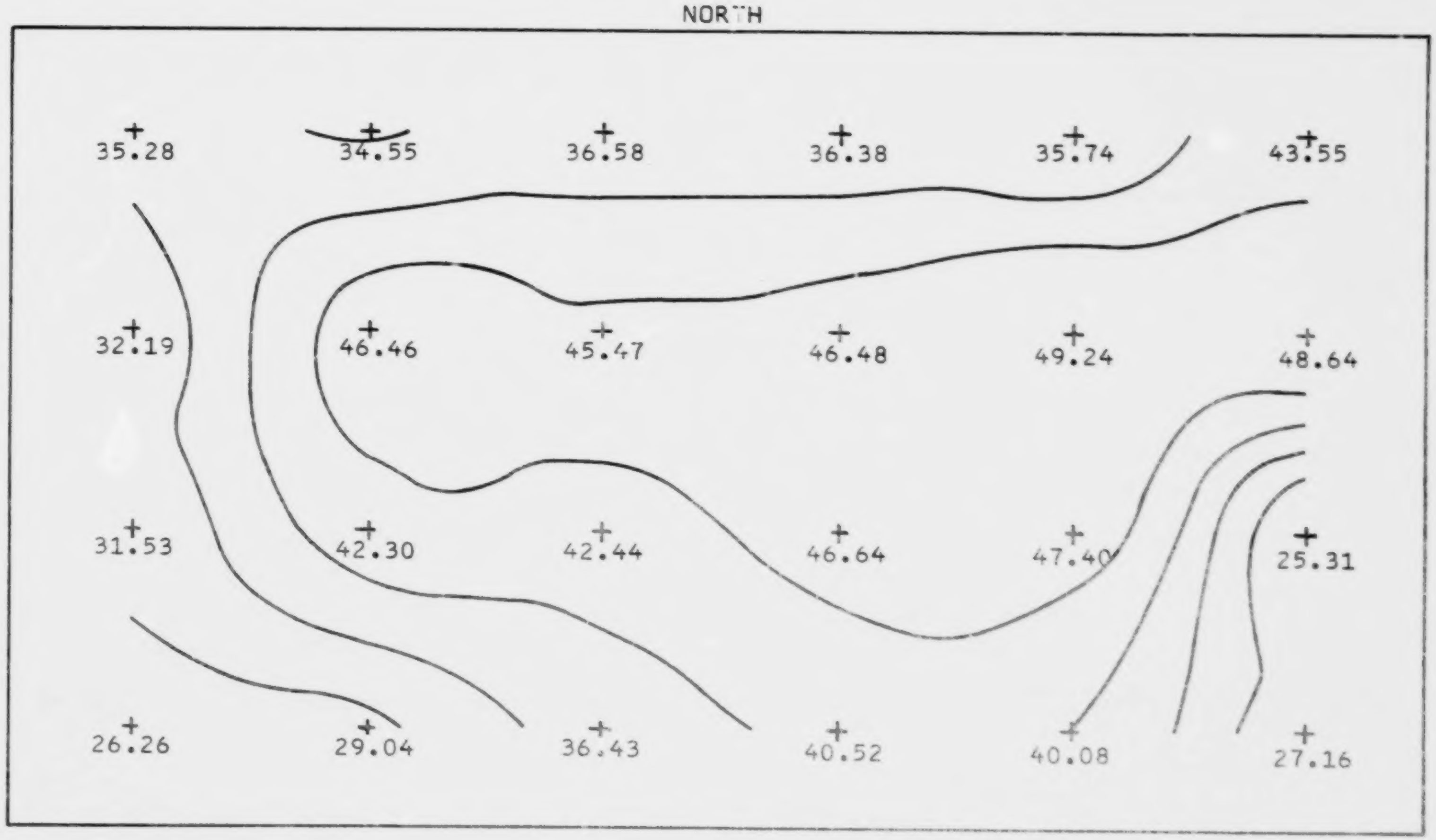
PLANE A-A EAST 12-11-70 TEST S603

CAO IN DUST SAMPLE - % INT = 5

Test Conditions

Unit load 129 MW, excess air 27%
Plane A-A avg. CaO in dust 29.69%
Secondary air dampers balanced
Injection at upper rear @ 0°
Fredonia limestone @ 1.7 stoich.

FIGURE 55



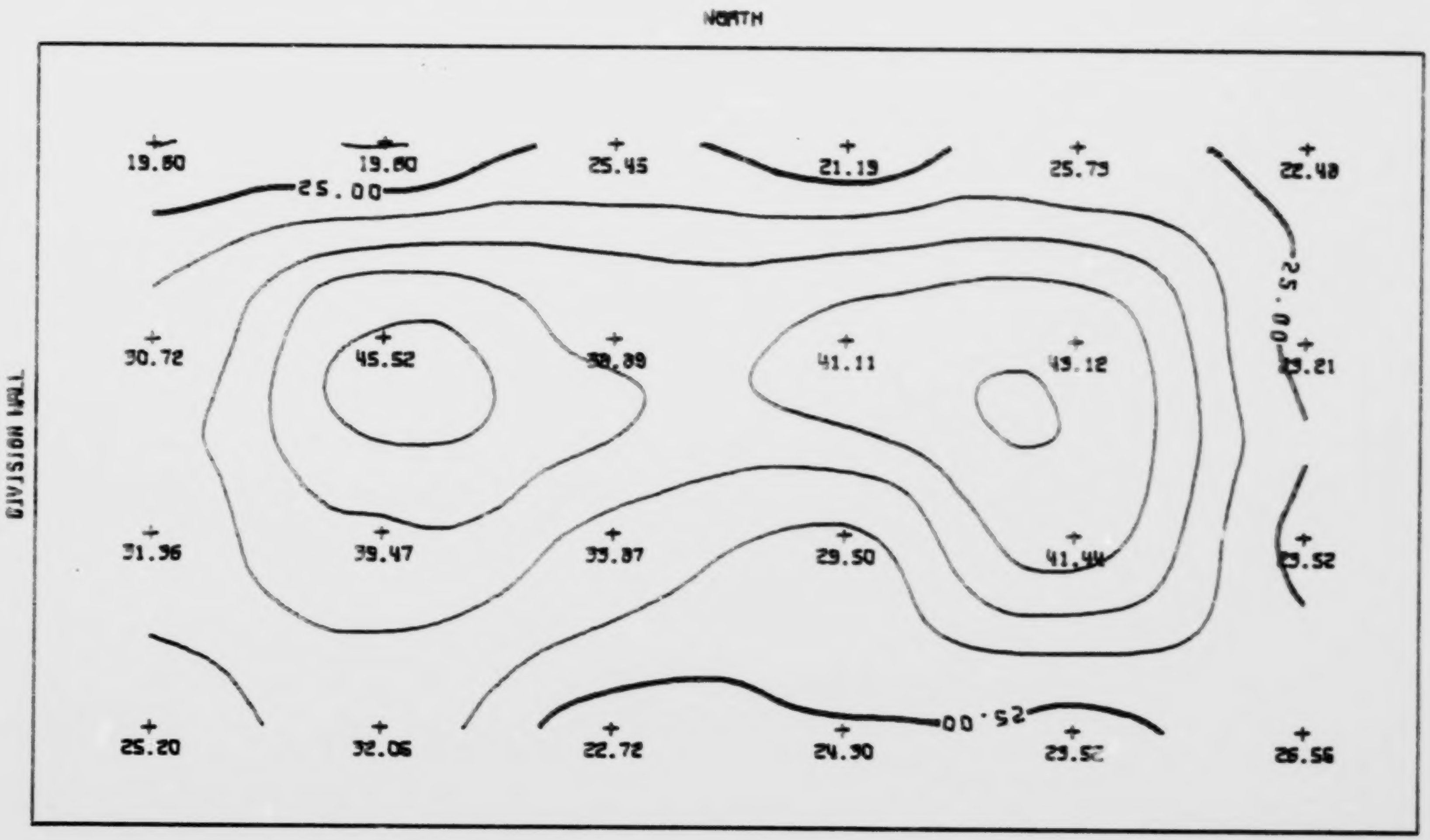
PLANE A-A EAST 12-3-70 TEST S601

CAO IN DUST SAMPLE - % INT = 5

Test Conditions

Unit load 129 MW, excess air 25%
Plane A-A avg. CaO in dust 38.57%
Secondary air dampers balanced
Injection at lower rear @ 0°
Fredonia limestone @ 1.7 stoich.

FIGURE 56



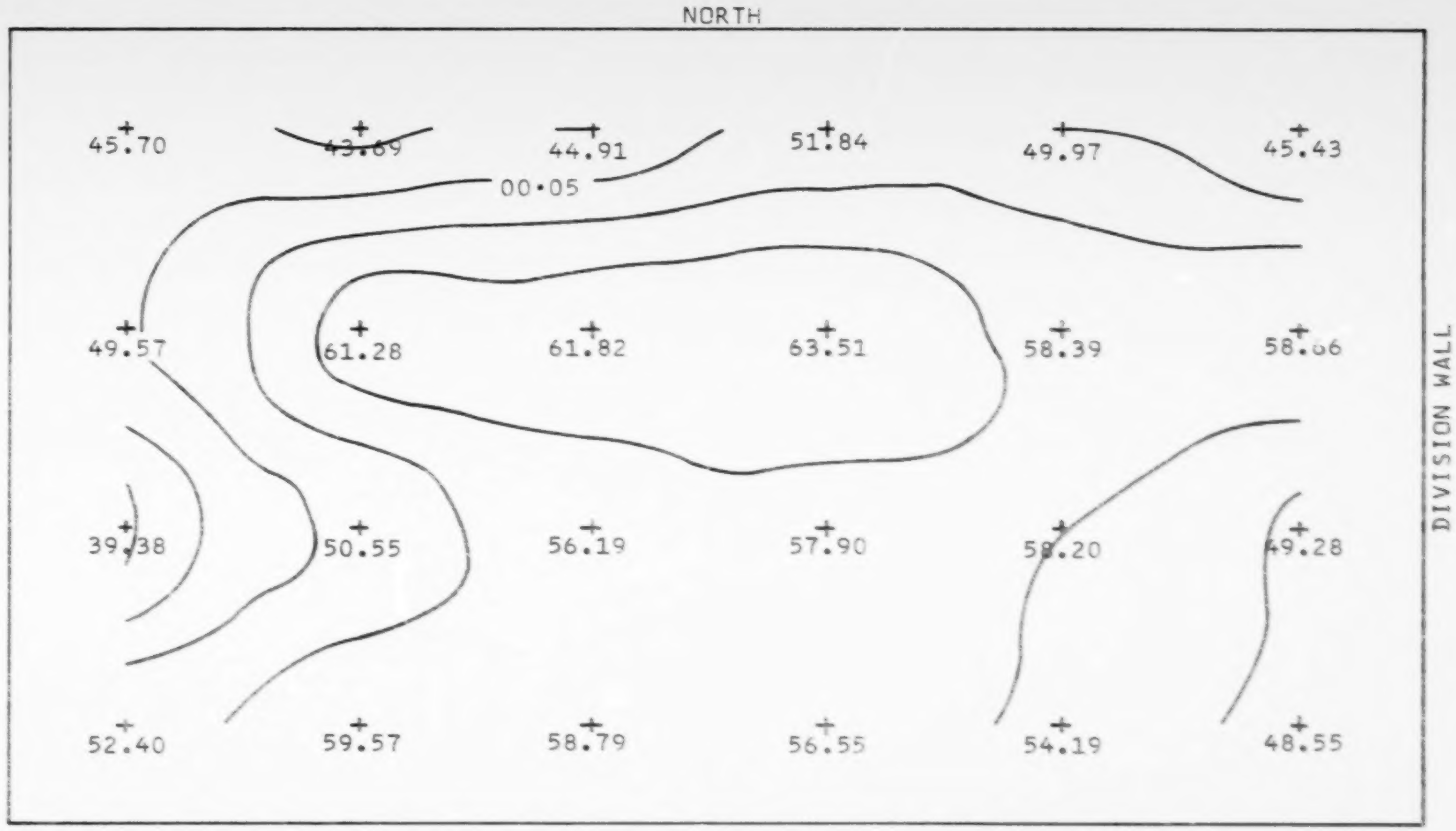
PLANE A-A EAST 12-11-70 TEST S602

CAO IN DUST SAMPLE - % INT = 5

Test Conditions

Unit load 129 MW, excess air 27%
Plane A-A avg. CaO in dust 29.59%
Secondary air dampers balanced
Injection at front @ 0°
Fredonia limestone @ 1.22 stoich

FIGURE 57



PLANE A-A WEST 2-9-71 TEST S201

CAO IN DUST SAMPLE-% INT = 5

Test Conditions

Unit load 140 MW, excess air 20%
Plane A-A avg. CaO in dust 53.18%
Secondary air dampers balanced
Injection at front end upper rear
Fredonia limestone

Injection velocity was variable within a 60 to 130 feet per second range as determined by whether one or two air compressors were in operation. Momentum of the injected limestone must be sufficient to allow jet penetration into the main bulk of furnace gas and the only measureable way to assess this is by CaO distribution. Analysis showed that injection velocity alone did not significantly affect dust distribution over the range tested. As mentioned earlier, steam assistance was used but it did not appear to help SO_2 removal rates.

g. Dust Distribution Changes with Burner Damper Settings

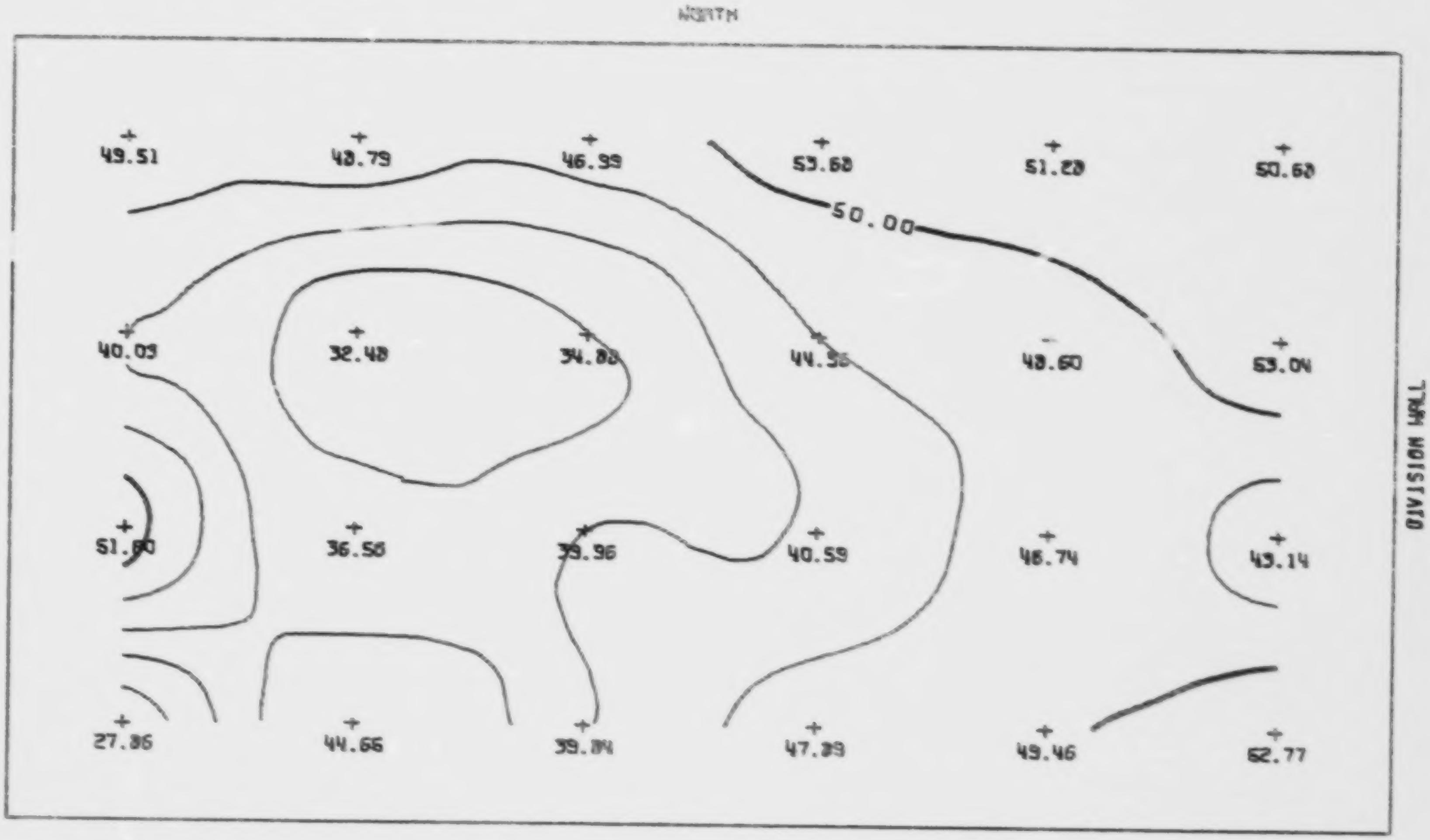
The next series of dust profiles was run with the objectives of determining the influence of burner secondary air damper settings on the dust distribution pattern. The plane A-A profile shown in figure 58 was developed with dampers of all eight burners as nearly balanced as possible. (See figure 64 for burner arrangement.) The profile shown in figure 59 was run with dampers of the top 2 burners (west furnace) set "air lean" and the other 6 burners in the balanced conditions. The third profile (figure 60) was run with the left column of 4 burners set "air rich" and the right column of 4 burners set "air lean." Comparison of figures 58 and 59 show that there is no detectable change in dust profile when the top row dampers are changed. However, changing both columns of dampers does significantly affect the dust profiles, as shown in figures 59 and 60. Although selective adjustment of secondary air dampers did produce identifiable changes in dust profiles there were times when these changes occurred without damper adjustments. On other occasions some damper adjustments had no noticeable effect.

During this series a number of oxygen traverses were made at the plane A-A with different damper settings. The oxygen profiles exhibited the same variability as observed for temperature, velocity, and dust. A typical profile is shown in figure 61. No influence by damper settings on oxygen profiles was noted.

4. CONCLUSIONS

Study of the numerous dust profiles generated during this dust distribution study shows, with ample evidence, that under all injection modes, furnace turbulence is the variable which has the greatest effect on dust distribution.

Even with the wide operating range covered by the present injection system, it is concluded that injection parameters of angle, velocity and location had little or no influence on dust distribution in plane A-A. Once the limestone is injected into the furnace it quickly mixes with the gas and assumes the same flow path as these combustion gases. This conclusion is supported by statistical treatment of the lime concentration profiles in the plane A-A. Based on results from 78 tests, the profiles of figure 62 show the average west-to-east and north-to-south lime concentrations at plane A-A, as obtained from the dust distribution study. These profiles remain stable even though injection conditions are varied. This suggests that under boiler operating conditions controlled as closely as possible there is a persistent gasflow pattern in the furnace which persists despite changes in injection location, angle and velocity.



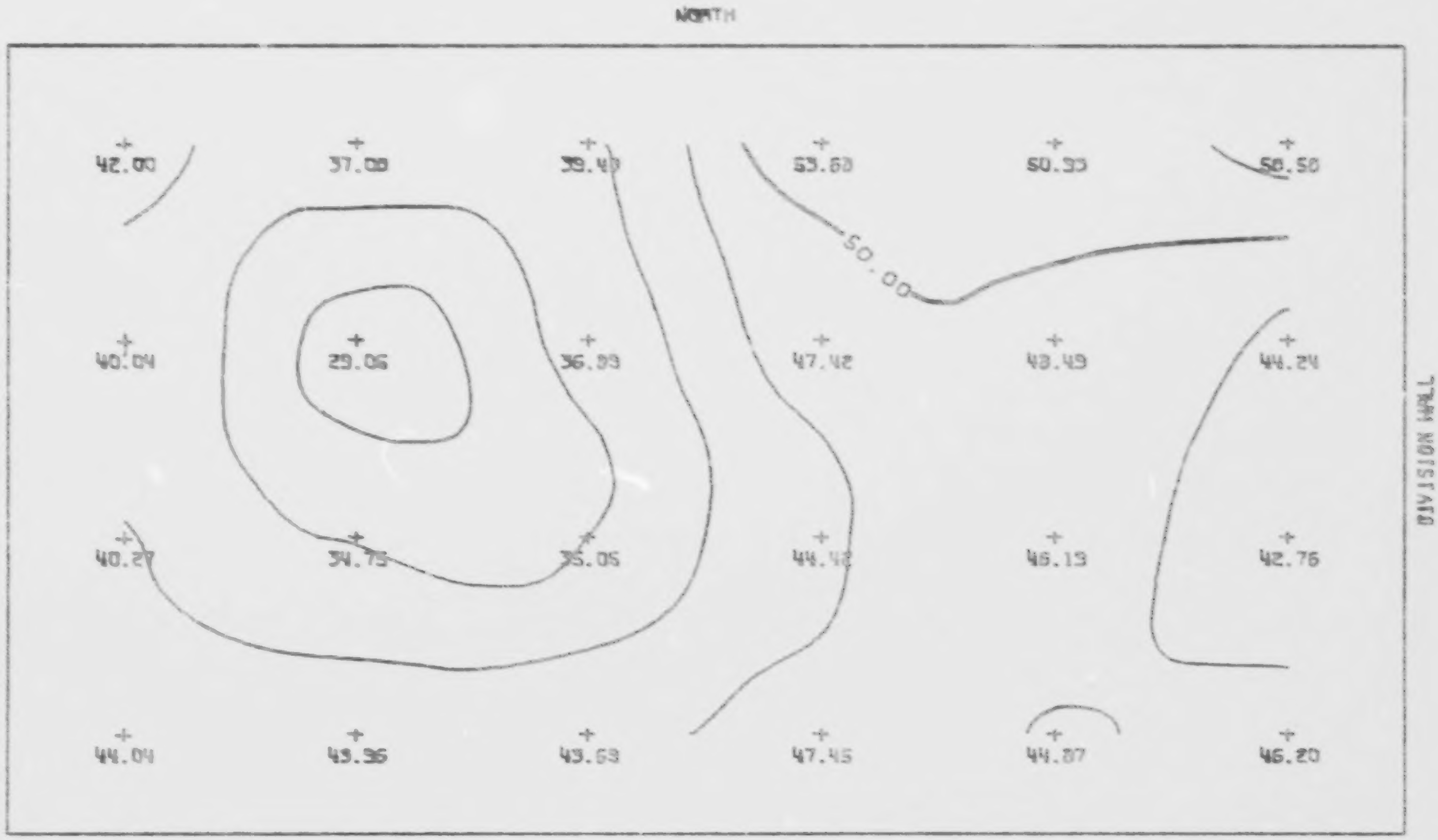
PLANE A-A WEST 12-30-70 TEST S901

CAO IN DUST SAMPLE - % INT = 5

Test Conditions

Unit load 140 MW, excess air 20%
Plane A-A avg. CaO in dust 44.83%
Secondary air dampers balanced
Injection at lower rear @ 0°
Fredonia limestone @ 2.85 stoich.

FIGURE 58



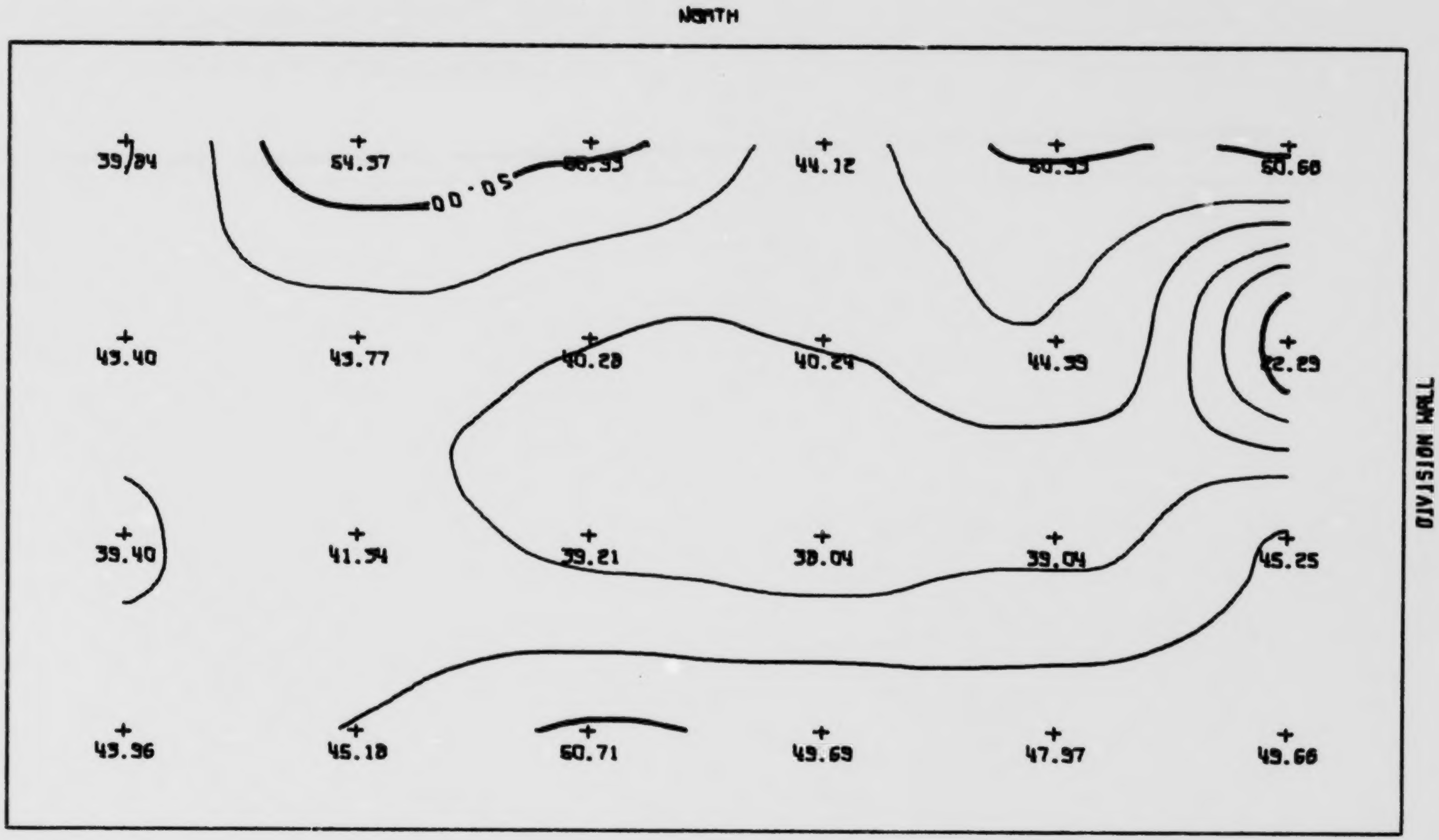
PLANE A-A WEST 12-30-70 TEST S902

CAO IN DUST SAMPLE - % INT = 5

Test Conditions

Unit load 140 MW, excess air 20%
Plane A-A avg. CaO in dust 44.31%
Secondary air dampers unbalanced
Injection at lower rear @ 0°
Fredonia limestone @ 3.35 stoich.

FIGURE 60



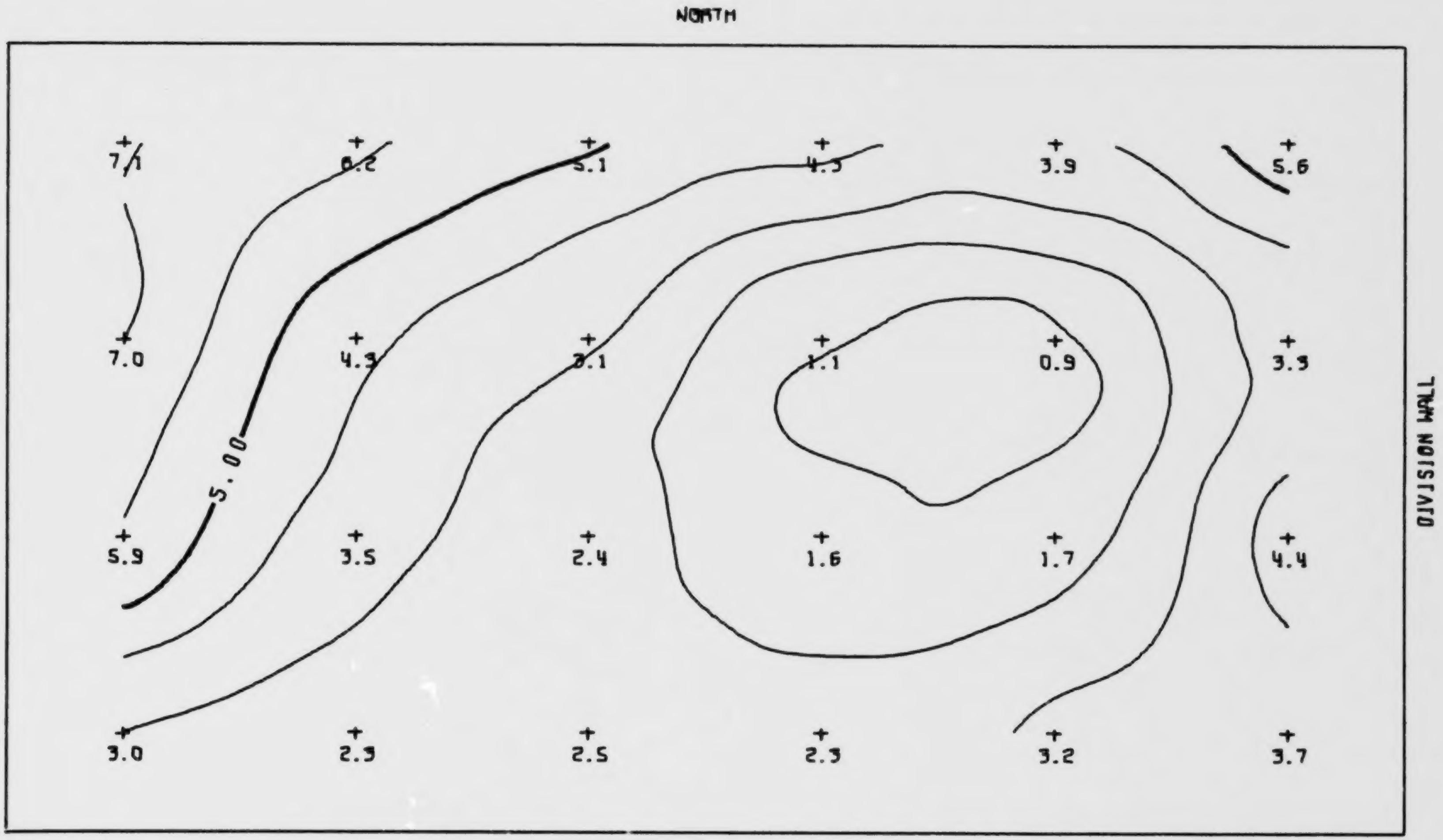
PLANE A-A WEST 12-30-70 TEST S903

CAO IN DUST SAMPLE - % INT = 5

Test Conditions

Unit load 140 MW, excess air 20%
Plane A-A avg. CaO in dust 43.94%
Secondary air dampers unbalanced
Injection at lower rear @ 0°
Fredonia limestone @ 2.94 stoich.

FIGURE 61



PLANE A-A WEST 01-13-71 TEST S905

O2 IN GAS - % INTERVAL = 1.0

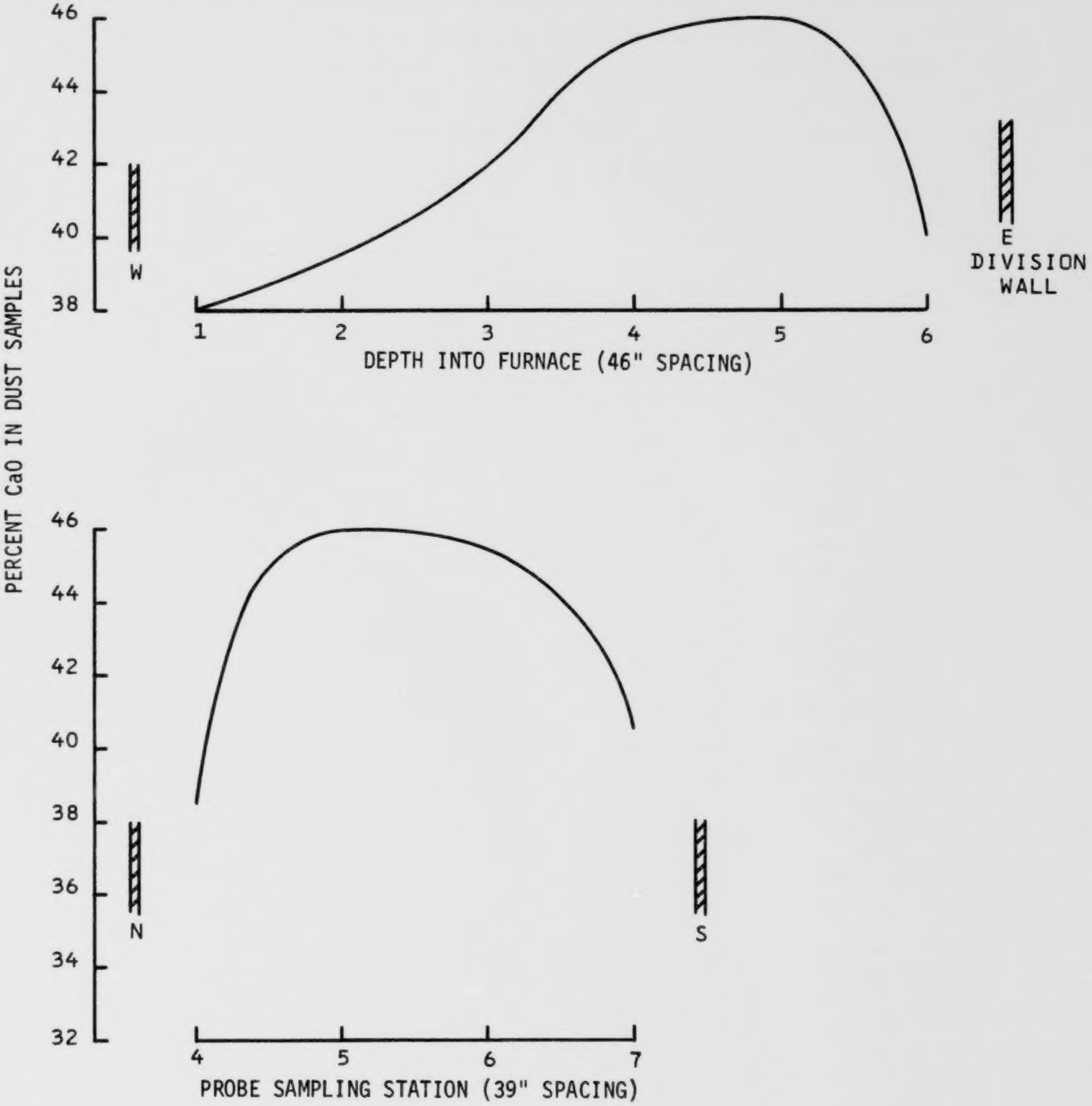
Test Conditions

Unit load 142 MW, excess air 22%
Plane A-A avg. O_2 3.7%

FIGURE 62

CaO DISTRIBUTION PROFILE TRENDS
SHAWNEE UNIT 10

WEST-TO-EAST AND NORTH-TO-SOUTH TRENDS AT PLANE A-A
FOR UPPER REAR, LOWER REAR, AND FRONT INJECTION



Since lime dust distribution is controlled by furnace turbulence, the attempt at imposing ouside control over dust distribution yields little effect. Under normal conditions, it is not practical or even possible to control all the variables which may influence turbulence. However, it is reasonable to expect that combustion turbulence also controls fly ash distribution and resulting gas patterns, therefore, it may not be desirable to impose outside control in attempts to modify existing dust distribution patterns with respect to SO_2. The similarity in patterns of the average lime concentration profile of figure 62 and the average SO_2 concentration profile of figure 26 suggests that the lime and SO_2 are distributed in essentially the same way.

Injection locations must be considered such that sufficient time is available for mixing and maximum time is available in the temperature range that accomplishes the CaO reaction with SO_2.

E. PHASE III, PROCESS OPTIMIZATION

1. OBJECTIVES

The purpose of Phase III tests was to optimize additional process variables by determining the effects on SO_2 removal while varying limestone type, particle size, injection angle and velocity, furnace excess air and boiler load.

Early research work on pilot plants and full-scale facilities that was conducted outside the United States by Zentgraf[3], Ishihara[4], Tanaka[6], and by Kruel and Juntgen[7] identified the major process variables for dry limestone injection, viz., retention time at temperature, particle size, stoichiometry, and limestone type. Goldschmidt[8] also identified these except for particle size which was relatively constant for his tests.

2. APPROACH

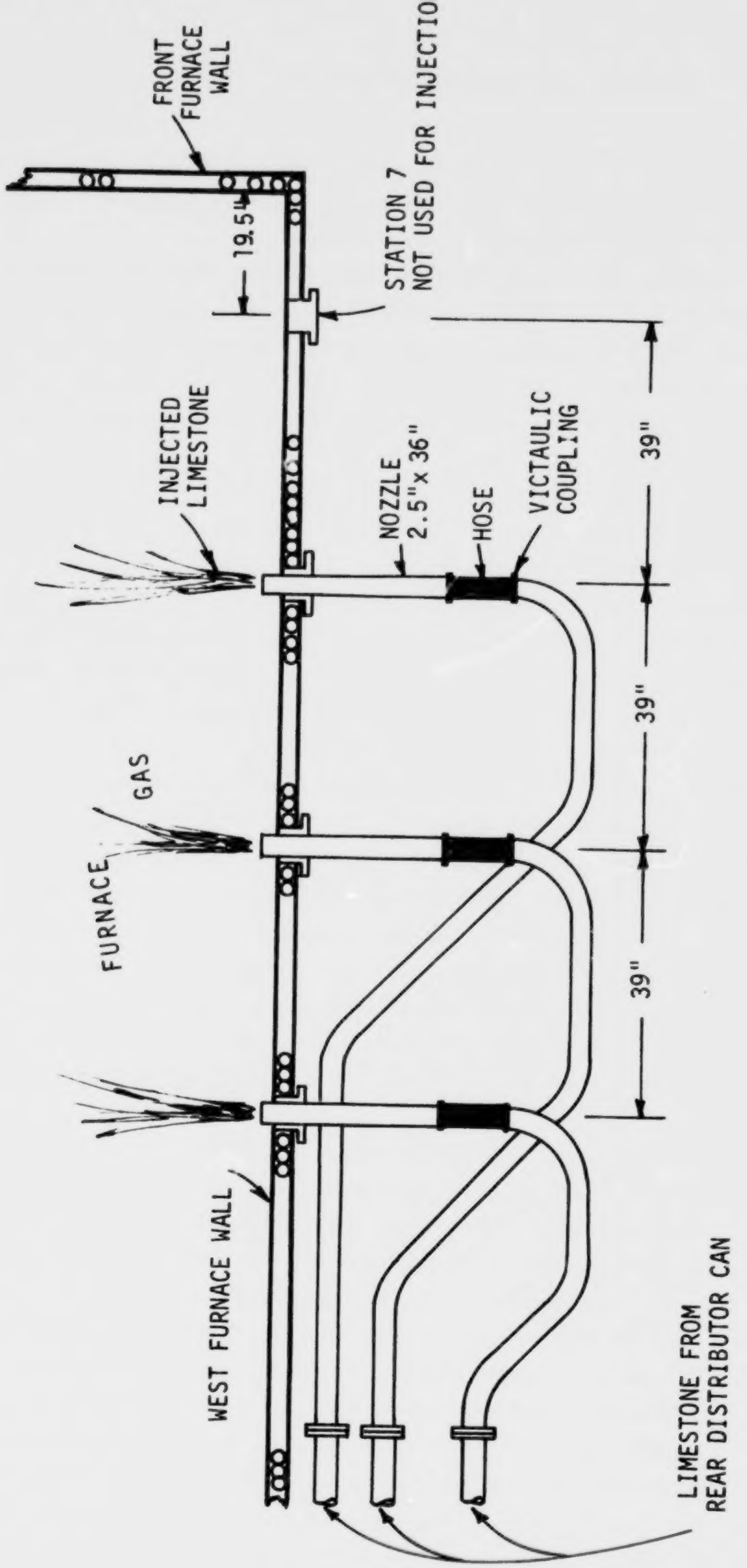
Full-scale test results obtained at Shawnee during Phases I and II identified limestone injection location and stoichiometry as two important variables which significantly influence SO_2 removal efficiency. Injection location influences retention time and temperature to which limestone particles are subjected during calcination. These factors determine whether or not deadburning of stone will occur. It was recognized that higher stoichiometry would increase SO_2 removals but at less efficient rates as stoichiometry increased.

Selection of the limestone injection locations for these optimization tests was based on Phase I test results which showed that stone injected at the lower rear was less reactive than stone injected at the upper rear. At the lower rear the particles were probably in contact with maximum temperature gas (2700 °F) and essentially the same or perhaps a few hundred degrees lower at the upper rear (not measured due to inaccessibility). Temperatures at the plane A-A were measured and ranged from 1800-2300 °F. To obtain lower injection temperatures it was decided to relocate nozzles to the plane A-A which is 27 feet above lower rear, 12 feet above upper rear and 17.5 feet above the front injection elevation. Only 3 of the 4 available ports on each side of the furnace were used for injection.

Limestone injection through plane A-A ports would provide the lowest injection temperatures available on Unit 10 without major redesign of the system. Piping was fabricated and installed to connect the rear distributor with nozzles located in test sampling stations 4, 5, and 6 (see figure 63), east and west sides. This left only the two probes at sampling station 7 available for temperature and velocity correlation.

Compared with injection at the upper rear, use of plane A-A for injection would further reduce mixing time of limestone and gas perhaps by 0.2 sec. Only 23 feet of mean flow path in the reaction zone exist before reactants enter the convection pass where temperature (approx. 1700 °F) and reactivity drop rapidly. Concern existed whether adequate mixing would result. Therefore, sampling probes were also installed at existing access locations (i.e., future soot blower and inspection doors) along the vertical plane B-B, shown in figure 11. Unfortunately, available ports in plane B-B did not

FIGURE 63


FRONT FURNACE WALL
STATION 7 NOT USED FOR INJECTION
19.5"
INJECTED LIMESTONE
NOZZLE 2.5"x 36"
HOSE
VICTAULIC COUPLING
39"
39"
39"
FURNACE GAS
WEST FURNACE WALL
LIMESTONE FROM REAR DISTRIBUTOR CAN

REVISED INJECTION NOZZLE PIPING FOR PLANE A-A

PLAN VIEW AT WEST SIDE

permit uniform sampling of temperature, velocity and dust in this area thus reducing value of data taken here. Test results would show that dust sampling at plane B-B suggest reasonably uniform mixing of limestone and flue gas entering the convection passes. Possibly the division wall which separates Unit 10 into east and west furnaces and which ends within the secondary superheater pendants induces gas stratification through the convection passes. This stratification is enhanced as gas flows back through secondary superheater and reheater sections.

Concurrent with full-scale testing at Shawnee the Control Systems Division of EPA had a contract with West Virginia University for model studies covering an "Experimental Investigation of the Penetration and Dispersion Phenomena in the Limestone Injection Study"[5]. Data obtained from Shawnee was used for some of the test work undertaken in this contract. Although some correlation with full-scale results was obtained, development of a mathematical model to predict injection flow patterns in a full-scale furnace was not completed.

Test Design

Development of the Phase III test program required the grouping of variables into two main types: controlled and uncontrolled. Those that were controlled included certain boiler factors that were maintained or held as constant as possible within safe operational limits during given test runs. The other major group consisted of variables that were measured but were generally uncontrolled. Variables in each of these groups are as follows:

TABLE 3

CONTROLLED AND UNCONTROLLED VARIABLES

CONTROLLED		UNCONTROLLED
FIXED	MAINTAINED	MEASURED
Injection angle	Boiler load	Ash fusion temperature
Injection velocity	Burner balance	Injection temperature
Particle size	Damper settings	Reaction zone temperature
Stoichiometry	Excess air	% sulfur in coal
Limestone type		

The variables of stoichiometry and particle size required little effort to define and quantify. This is in contrast to the difficult problem of defining and measuring particle retention time in the reaction zone since this interval depends on injection conditions, boiler load, and excess air.

a. Limestone Selection

The approach toward limestone selection involved obtaining a type most suitable for Shawnee full-scale tests and finding representative types for potential use in other areas. The subject of Limestone Availability is covered in appendix I, section B.

Three different types of limestone were selected for Phase III tests. These were Fredonia (BCR* 2061), Michigan marl (BCR 2129), and oolitic aragonite (BCR 2208), the last two were identified as being especially reactive in bench scale tests. Limited tonnages of marl and aragonite were available for Shawnee tests. Aragonite was obtained from the Bahama Islands. Considerable research[9, 10, 11, 12, 13] on numerous limestones had been performed prior to selections for these tests.

Properties of Fredonia Valley (White) limestone (BCR 2061) were fully adequate for the Shawnee tests. The Fredonia Valley Quarries are located in Kentucky some 40 miles from the Shawnee plant so stone was trucked to the site. The quarry is an open face operation and has two high calcium ledges of white oolitic stone separated by a blue ledge. Reference 14 gives the composition of these ledges as follows:

Table 4

CHEMICAL COMPOSITION OF FREDONIA LIMESTONE LEDGES

% Composition

Ledge	$CaCO_3$	$MgCO_3$	SiO_2	Fe_2O_3	Al_2O_3	S	P
top 36'	98.2	0.72	0.82	0.10	0.09	.001	.008
lower 30'	97.2	1.78	0.72	0.17	0.08	.023	.010

Samples of Fredonia Limestone (BCR 2061) delivered for Shawnee tests also contained traces of these compounds, expressed in wt. percent:

TiO_2	0.03
Na_2O	<0.02
K_2O	<0.1
MnO_2	<0.03

Limestone particle size, a controlled variable, was determined by settings of the gyrotor classifier to yield the following sizes, typical for Fredonia:

Mesh	Classifier Setting 20% % Passing	Classifier Setting 98% % Passing
-30	99.5%	100%
-50	96.5%	100%
-100	83.9%	99.9%
-200	69.2%	86.7%

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*Bituminous Coal Research

TABLE 5

CHEMICAL COMPOSITION AND PARTICLE SIZE DISTRIBUTION OF THREE DIFFERENT LIMESTONES INJECTED IN PHASE III TESTS

BCR No.	2208	2061	2129
Field Lab. No.	12700	11598	12315
	Aragonite	Fredonia Limestone	Michigan Marl
Chemical Composition:			
% Ing. Loss (Moist. + CO_2)	43.8	43.0	41.6
SiO_2	1.8	1.0	7.6
Al_2O_3	0.3	0.1	1.2
Fe_2O_3	0.1	0.2	0.6
CaO	52.2	52.3	43.8
MgO	0.8	0.5	2.3
Sp. gravity	2.67	2.49	2.55

BAHCO Particle Size: (as fed to the boiler)

Size Microns	% Less Than	Size Microns	% Less Than	Size Microns	% Less Than
5.9	27.1	6.0	38.7	6.0	50.5
8.8	38.3	8.9	50.9	9.0	60.7
12.0	47.1	12.2	57.9	12.3	69.6
16.4	57.3	16.7	63.9	16.8	78.3
21.9	71.3	22.2	72.6	22.4	86.0
26.7	78.4	27.2	76.5	27.4	89.2
29.6	80.6	30.1	78.2	30.3	90.4

b. Coal Supply

Unit train coal delivery during the test period greatly lessened the wide swings in properties, especially sulfur content which can result in test stoichiometries exceeding those planned.

An eastern Kentucky low sulfur coal with less than 0.8% sulfur was purchased specifically to determine the effect of low SO_2 concentration on SO_2 removal efficiency.

Coal was sampled and analyzed for total sulfur and ash contents. Some samples received proximate analysis and determination of ash fusion temperatures. Table 6 is a summary of coal contract data as pertains to consumption during phases I, II, and III.

c. Boiler Load

Furnace gas conditions are influenced mostly by load. Previous testing revealed process sensitivity to secondary air damper settings and to the operating burner configurations. Low load (75 MW) and variations in burner configurations would result in lower gas temperatures and velocities, consequently, longer particle residence time in the reaction zone. Burners are arranged as shown in figure 64. Relative position of the flame can be raised or lowered perhaps 15 feet, depending on whether A and B-row mills or C and D-row mills are suppling the fuel. Secondary air dampers on the unused burners were closed to further reduce gas velocity. These were the possible firing modes used during optimization tests in order to learn if load, as a controlled variable, would influence SO_2 removal efficiency.

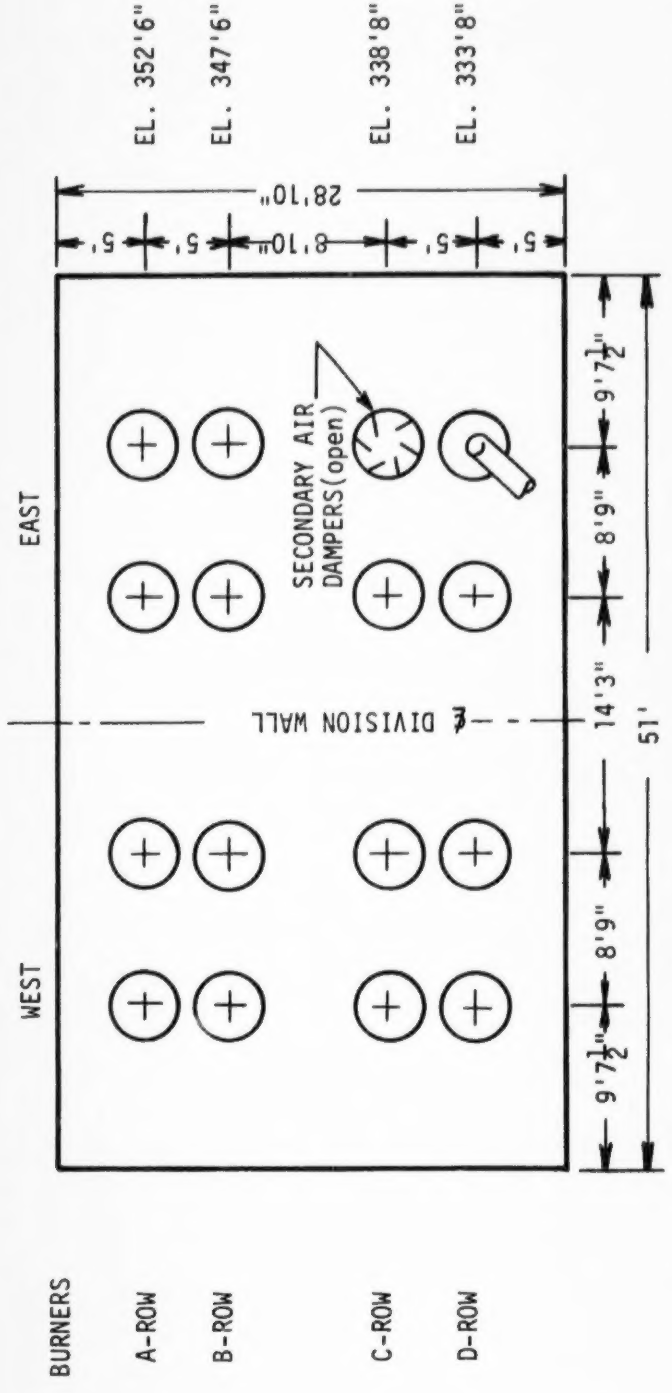
Boiler load was maintained as constant as possible during the initial series of tests on Fredonia limestone to prevent the large influence of load from obscuring effects of other variables. Following the controlled variable optimization test runs the boiler load was reduced incrementally to determine effects on SO_2 removal.

d. Injection Angle and Velocity

It was decided that at the plane A-A, smaller injection angles (25° vs. 45°) would be used because it was felt that at this plane the injection angle would have a greater effect than that previously recognized for this variable. Velocity was varied during these tests since residence time at temperature would be altered by going to the plane A-A thus jet penetration was important as a controlled variable.

FIGURE 64

SHAWNEE UNIT 10
BURNER ARRANGEMENT


EL. 352'6"
EL. 347'6"
EL. 338'8"
EL. 333'8"
28'10"
5'
5'
8'10"
5'
5'
EAST
WEST
SECONDARY AIR DAMPERS(open)
℄ DIVISION WALL
9'7½"
8'9"
14'3"
8'9"
9'7½"
51'
BURNERS
A-ROW
B-ROW
C-ROW
D-ROW

FRONT ELEVATION
OF WINDBOX

TABLE 6

COAL CONTRACT DATA

Consumption Date	Coal Contract No.
11-24-70	70P-81-T10
11-25-70	70P-81-T10
12-2-70	70P-81-T10
12-3-70	70P-81-T10
12-4-70	60P-90-T17
12-8-70	70P-81-T10
12-10-70	70P-81-T10
12-11-70	71P-92-E80 and 70P-81-T10
12-15-70	70P-81-T10
12-16-70	70P-81-T10
12-30-70	71P-41-T19
12-30-70	71P-41-T19
1-5-71	71P-41-T19
1-7-71	70P-81-T10
2-9-71	70P-81-T10
2-11-71	70P-49-T35
2-16-71	70P-81-T10
2-26-71	70P-81-T10
3-2-71	70P-81-T10
3-3-71	70P-81-T10
3-4-71	70P-81-T10
3-5-71	70P-81-T10
4-1-71	70P-81-T10
4-2-71	70P-81-T10
4-5-71	69P-70-T17
4-6-71	70P-81-T10
4-7-71	70P-81-T10
4-8-71	70P-81-T10
4-9-71	70P-81-T10
4-12-71	71P-97-E126
4-13-71	71P-41-T19
4-14-71	70P-81-T10
4-15-71	70P-81-T10
4-16-71	70P-81-T10
4-20-71	71P-41-T19
4-21-71	70P-96-T2
4-22-71	70P-81-T10
4-23-71	71P-41-T19 and 70P-81-T10
4-26-71	71P-72-E126 and 71P-92-E149
4-27-71	70P-81-T10
4-28-71	70P-81-T10
4-29-71	70P-81-T10
5-4-71	70P-81-T10
5-5-71	70P-81-T10
5-6-71	70P-81-T10
5-7-71	70P-81-T10
5-10-71	71P-92-E126
5-11-71	70P-81-T10
5-12-71	71P-41-T19 and 60-P-90-T17
5-13-71	70P-96-T2
5-14-71	70P-81-T10
5-20-71	71P-41-T19 and 70P-81-T10
5-21-71	70P-96-T2
5-24-71	70P-96-T2
5-25-71	70P-81-T10
5-26-71	70P-81-T10
5-27-71	70P-81-T10
5-28-71	70P-81-T10
6-3-71	70P-81-T10
6-4-71	70P-81-T10
6-7-71	60P-90-T17
6-8-71	60P-90-T17
6-9-71	Reclaim
6-10-71	70P-81-T10
6-11-71	60P-90-T17
6-15-71	70P-81-T10
6-23-71	70P-81-T10
6-24-71	70P-81-T10
6-25-71	70P-81-T10
6-28-71	62P-40-T17
6-29-71	62P-40-T17
7-10-71	Reclaim
7-12-71	Reclaim
7-13-71	70P-81-T10
7-14-71	Reclaim
7-15-71	Reclaim
7-19-71	71P-41-T19
7-20-71	62P-40-T17
7-21-71	71P-92-E126
7-22-71	70P-81-T10
7-23-71	70P-81-T10
7-24-71	70P-81-T10
7-26-71	70P-96-T2
7-27-71	70P-96-T2
7-28-71	71P-92-E149
8-9-71	71P-92-E126
8-10-71	71P-41-T19
8-11-71	70P-96-T2
8-13-71	71P-41-T19
8-14-71	71P-41-T19
8-15-71	71P-92-E126
8-16-71	71P-92-E126
8-17-71	71P-41-T19
8-18-71	70P-81-T10
8-19-71	71P-92-E126

NOTE: Phase II - November 24, 1970 through April 9, 1971
Phase III - April 12, 1971 through August 5, 1971
Phase IV - August 9, 1971 through January 10, 1972

Test Data Analysis

Numerous test possibilities required a statistical approach to selection of the variable combinations. Initial tests were to be run at 2 levels for each controlled variable in a full 2^4 factorial layout plus center point replication for a total of 20 tests. Operational considerations made it impracticable to change particle size frequently so a certain degree of nesting was required. Particle size was changed after every 4 runs; therefore, the sequence of particle sizes to be run was determined at random to be coarse, fine, coarse, and fine. At first, the 8 combinations within the 2 levels of particle size were completely randomized. Later, it was decided to alter the sequence to provide a complete half replication after 10 tests. This would provide maximum efficiency in distinguishing linear and quadratic trends in the first 10 tests as well as the full 20 tests. The effects of major variables were determined; uncontrolled but measured variables were evaluated through regression analysis.

Following the initial test block, 3 test blocks were run to characterize the effect of limestone type. Some special sensitivity tests were also made to determine effects of limestone type, boiler load, percent sulfur in coal and excess air. Normal coal deliveries, which can range from 1.0-5.5% sulfur content, and the normal range of excess air were two variables expected to show enough variation among tests to allow determination of their effect on SO_2 removal through regression analysis.

3. RESULTS

a. Summary

The 5 series of optimization tests are identified in table 7 and summarized in terms of selected variables and results in table 8. Note that marl (Series 2000) and argonite (Series 4000) tests were separated by a return to Fredonia limestone for low load tests (Series 3000). The highest stoichiometry obtained was 9.57X and occurred in Series 5000 with low sulfur coal. Statistical evaluations were carried out on all series in order to identify relative importance of controlled and uncontrolled parameters.

Table 7

OPTIMIZATION TEST SERIES IDENTIFICATION

Series	Limestone Type	Boiler Load (MW)	Test Period (1971)
1000	Fredonia	140	4/12 - 5/14
2000	Michigan marl	75	5/20 - 6/4
3000	Fredonia	75	5/24 - 5/27
4000	Aragonite	140, 75	6/7 - 6/25
5000	Fredonia	108-141	6/28 - 6/29

Table 8

OPTIMIZATION TESTS

Ranges of Selected Variables and Results

Optimization Series	1000	2000	3000	4000	5000
Limestone Injected	Fredonia	Marl	Fredonia	Aragonite	Fredonia
Boiler load, MW	35 tests @ 139-142 4 tests @ 131-138 3 tests @ 115-130	10 tests @ 139-142 5 tests @ 74-75	14 tests @ 73-75	11 tests @ 139-143 6 tests @ 75	8 tests @ 133-141 5 tests @ 108-114
Stoichiometry	0.57-5.06	0.80-6.93	0.63-4.10	0.77-5.76	1.61-9.57
% Excess Air East West	11-39 10-40	20-33 22-31	16-37 20-33	16-30 11-31	10-33 11-33
Particle Size Index	2.5-6.0	2.3-2.6	2.2-5.5	3.9-13.7	2.6-2.8
Injection Angle, Degrees	-25°, 0°, +25°	-25°, +25°	-25°, 0°	-25°, 0°	-25°
Injection Velocity, ft./sec.	36-92	59-92	44-92	32-89	42-92
% SO_2 Removal East West	3.3-32.6 6.9-40.0	6.3-62.6 7.9-75.5	9.3-41.6 10.5-46.5	5.7-35.3 4.8-34.0	9.1-38.1 8.9-43.3
Initial SO_2 Conc. (ppm) East West	860-3760 1120-3460	1280-2700 1280-2680	1880-2740 1920-2760	1940-2980 2040-3000	740-1100 740-1040
Limestone % Utilization East West	6.2-15.8 7.6-17.6	8.2-19.6 9.7-19.6	9.8-18.8 10.6-19.1	9.4-13.4 8.9-17.4	4.2-16.1 3.5-14.1

b. Optimization Tests

Series 1000

Fredonia limestone (BCR 2061) was injected for all tests and with few exceptions full load on Unit 10. Table 9 is a summary of results. The column on % SO_2 removal for east and west furnaces is based on ultraviolet (uv) analyzer readings of SO_2 concentrations taken at plane C-C before, during and after limestone injection. (As required for Method 3 calculation of SO_2 removal). The column on initial SO_2 concentration refers to values before starting injection. The suffix F and X on test numbers were preliminary indicators as to whether or not a test met operating criteria. Later analysis could not differentiate such designations.

The station 7 probes which are closest to the front wall of the furnace were the only ones available for the type of sampling previously obtained by all eight plane A-A probes. Attempts to verify the gas temperatures at station 7 by optical pyrometer measurements did not prove successful, with the optical readings generally higher.

Data on coal ash content and fusion temperatures for all optimization series tests is shown in table 10. Proximate coal analyses for all series appears in table 11.

Since particle size is an important controlled variable in the dry limestone injection technique, the data for coarse and fine sizes were plotted separately. Those tests with particle size index above 4.8 were plotted as coarse and those below 4.8 plotted as fine. About 58% of the coarse size and 87% of the fine size is -400 mesh.

Figure 65 is a plot of 19 tests using coarse grind. Note that 1X stoichiometry removed approximately 10% of the initial SO_2 present and 2X stoichiometry only 17%. Higher injection rates appeared to give even less SO_2 removal per unit stoichiometry. Figure 66 is a plot of 23 tests involving fine grind and includes the neutral point tests where medium size (50% gyrotor speed) stone was used. Again, the data shows a 10% SO_2 removal for 1X stoichiometric and continues linear to the highest injection rate tested on fine particle size, viz. 3.4X. Figure 67 is a composite plot of all 42 tests in the Series 1000.

The injection of fine particle size limestone resulted in better SO_2 removal efficiency at high stoichiometries than did coarse grind limestone. The increased surface area of fine grind particles would be more than enough to account for the better removal of fine grind over the coarse.

Figure 68 is a plot of SO_2 removal per unit stoichiometry (removal efficiency) versus stoichiometry for the series 1000 tests. Figure 69 is a plot of SO_2 Removal Efficiency vs. Limestone Utilization for series 1000 tests which had an initial SO_2 concentration that exceeded 1500 ppm.

Table 9

OPTIMIZATION TESTS
SUMMARY SHEET, SERIES 1000
Fredonia Limestone - Full Load
(42 Tests)

Test No.	Test Date	Unit Load MW	Stoich- iometry (1)	% Excess Air E	% Excess Air W	Particle Size Index (1)	Injection Conditions Angle Degrees (1)	Injection Conditions Vel. F.P.S. (1)	Injection Conditions Com- pressors (2)	% SO$_2$ Removal E	% SO$_2$ Removal W	Initial SO$_2$ ppm (3) E	Initial SO$_2$ ppm (3) W	Limestone % Utilized (4) E	Limestone % Utilized (4) W
1011F	4-12-71	140	0.88	33	38	6.0	-25°	58	1C	7.5	6.9	3340	3260	11.3	15.9
1012F	4-12-71	140	0.91	36	36	5.1	-25°	58	1C	11.3	8.0	3380	3120	14.6	18.9
1013X	4-13-71	140	1.09	27	20	5.4	-25°	64	1C	8.8	10.9	1720	1800	15.8	14.1
1021F	4-13-71	141	2.50	27	21	5.8	+25°	56	1C	23.9	25.3	1760	1800	10.8	10.5
1031F	4-13-71	141	1.01	28	27	5.8	+25°	82	2C + S	8.3	12.5	1480	1760	14.8	15.5
1022F	4-14-71	141	5.06	24	25	6.0	+25°	42	1C	29.1	31.9	1900	1680	7.8	11.7
1023X	4-14-71	137	2.88	25	25	5.9	+25°	57	1C	26.0	33.1	1360	1320	9.5	8.7
1032X	4-15-71	140	0.90	24	24	5.4	+25°	92	2C + S	8.4	12.1	1420	1360	10.6	12.6
1041F	4-16-71	140	2.69	23	25	4.6	-25°	69	2C + S	25.5	33.3	860	1120	8.2	9.8
1051X	4-16-71	140	2.10	25	27	4.8	0°	70	2C	23.5	32.8	1060	1200	8.9	11.4
1061F	4-20-71	140	3.13	23	25	3.3	+25°	61	2C + S	12.8	21.1	1420	1420	9.0	11.4
1071F	4-20-71	140	0.57	24	24	2.8	-25°	84	2C + S	9.0	9.0	1280	1280	12.5	16.1
1091F	4-21-71	140	0.81	24	26	2.7	+25°	62	1C	10.2	10.2	1960	1960	15.2	15.3
1062X	4-22-71	140	2.85	23	25	2.8	+25°	54	2C + S	20.8	31.1	1520	1520	9.7	12.4
1072X	4-22-71	140	0.83	24	24	2.6	-25°	85	2C + S	3.3	12.5	1600	1620	13.4	16.8
1092X	4-22-71	140	0.86	24	25	2.7	+25°	63	1C	5.7	11.6	1860	1720	14.4	16.0
1081F	4-23-71	140	1.95	22	24	2.6	-25°	48	1C	10.4	18.8	2940	2920	8.5	9.5
1101F	4-23-71	140	2.09	24	22	4.5	0°	56	2C	11.5	23.7	2220	2180	8.5	11.4
1151X	4-26-71	140	1.86	17	17	4.4	0°	46	2C	15.1	15.1	3040	3100	7.8	8.9
1111X	4-26-71	140	0.85	22	24	5.7	-25°	73	2C + S	9.3	9.3	2740	2800	11.6	13.0

Notes:
1. Major Test Variable
2. 1C - one compressor
   2C - two compressors
   2C + S - two compressors plus steam
3. Concentration before limestone injection
4. Based on analysis of samples from plane C-C
5. Load drop due to mill repair

Table 9 (continued)

Test No.	Test Date	Unit Load MW	Stoich-iometry	% Excess Air E	% Excess Air W	Particle Size Index (1)	Injection Conditions Angle Degrees (1)	Injection Conditions Vel. F.P.S. (1)	Injection Conditions Com-pressors (2)	% SO_2 Removal E	% SO_2 Removal W	Initial SO_2 ppm E (3)	Initial SO_2 ppm W (3)	Limestone % Utilized E (4)	Limestone % Utilized W (4)
1112F(5)	4-27-71	115	2.88	33	33	6.3	-25°	47	2C + S	21.8	21.8	2400	2400	9.6	17.6
1121X	4-28-71	140	2.83	25	23	5.5	+25°	45	2C + S	21.9	23.9	1980	1900	9.7	11.7
1042X	4-28-71	141	2.98	22	15	6.4	-25°	42	2C + S	18.8	24.5	1980	1900	9.2	11.5
1141F	4-29-71	140	4.30	24	25	6.0	-25°	44	1C	20.0	25.4	1820	1720	9.0	12.0
1131X	4-29-71	140	1.10	24	26	6.0	+25°	64	1C	9.2	9.4	1580	1600	11.8	13.3
1142F	5-04-71	140	4.23	26	24	5.1	-25°	49	1C	25.3	25.0	1720	1740	7.8	8.5
1161X	5-04-71	140	2.97	23	26	2.6	+25°	50	1C	29.6	33.9	1500	1520	10.0	9.1
1171X	5-05-71	141	1.07	25	24	2.8	-25°	60	1C	11.9	17.3	2160	2160	11.3	12.6
1181X	5-05-71	142	3.15	20	24	2.5	-25°	48	2C + S	28.6	38.3	1780	1700	8.6	10.4
1191F	5-06-71	140	0.81	26	24	2.7	+25°	77	2C + S	12.1	15.1	1760	1720	10.9	12.3
1192X	5-06-71	140	1.28	24	24	2.6	+25°	71	2C + S	8.8	13.3	3000	2840	10.9	14.8
1082F	5-07-71	141	2.45	24	24	2.6	-25°	41	1C	16.6	30.0	2740	2560	9.0	11.6
1201X	5-07-71	142	2.18	22	24	4.4	0°	52	2C	13.5	22.0	2400	2200	10.8	13.6
1102X	5-10-71	140	2.20	26	24	4.2	0°	49	2C	18.6	19.2	2600	2920	8.7	10.3
1152X	5-10-71	140	1.75	26	24	4.3	0°	56	2C	16.3	18.8	2460	2660	8.5	7.6
1113F	5-11-71	141	1.71	24	22	6.0	-25°	72	2C + S	18.3	17.5	2180	2280	9.2	12.5
1143F	5-11-71	141	4.60	24	22	5.4	-25°	36	1C	18.4	25.7	2460	2480	9.0	9.8
1144F	5-12-71	115	3.59	24	23	5.0	-25°	46	1C	27.7	31.0	2160	2320	9.3	9.5
1182F	5-12-71	117	3.38	25	22	2.7	-25°	49	2C + S	30.7	40.0	2180	2280	8.8	10.2
1183F	5-13-71	132	1.85	11	10	2.7	-25°	45	2C + S	7.8	10.6	3760	3460	7.2	9.6
1184F	5-13-71	131	2.00	11	10	2.7	-25°	45	2C + S	10.1	13.8	3360	3160	6.9	7.8
1185X	5-14-71	138	3.27	39	40	2.7	-25°	55	2C + S	32.6	35.5	1480	1440	6.2	9.5

Notes:
1. Major Test Variable
2. 1C - one compressor
   2C - two compressors
   2C + S - two compressors plus steam
3. Concentration before limestone injection
4. Based on analysis of samples from plane C-C
5. Load drop due to mill repair

Table 10

COAL ASH CONTENT
AND FUSION TEMPERATURES

Optimization Tests

Test No.	Date	% Ash[1]	Ash Fusion Temp. °F[2]
1013 X	4-13-71	12.9	2190
1032 X	4-15-71	12.9	2250
1051 X	4-16-71	11.8	2210
1062 X	4-22-71	15.6	2260
1072 X	4-22-71	14.4	2170
1092 X	4-22-71	14.5	2160
1151 X	4-26-71	13.7	2020
1111 X	4-26-71	14.1	2030
1121 X	4-28-71	12.8	2170
1042 X	4-28-71	13.0	2160
1131 X	4-29-71	13.7	2160
1161 X	5-04-71	11.7	2190
1171 X	5-05-71	12.7	2100
1181 X	5-05-71	13.7	2170
1192 X	5-06-71	23.4	2180
1201 X	5-07-71	14.3	2130
1102 X	5-10-71	13.5	2060
1185 X	5-14-71	14.3	2200
2020 X	5-20-71	14.9	2260
2010 X	5-20-71	18.3	2110
2030 X	5-21-71	14.4	2120
2040 X	5-21-71	14.1	2150
2050 X	5-21-71	14.6	2130
3021 X	5-24-71	15.4	2110
3041 F	5-24-71	16.8	2130
3011 X	5-24-71	18.8	2080
3051 X	5-25-71	15.2	2150
3071 X	5-25-71	14.8	2120
3061 X	5-25-71	14.3	2180
3081 F	5-25-71	14.3	2160
3012 F	5-26-71	14.0	2130
3031 F	5-26-71	14.1	2140
3022 F	5-26-71	13.9	2120
3091 X	5-27-71	14.8	2160
3111 F	5-27-71	17.0	2070
3101 X	5-27-71	17.8	2050
3121 X	5-27-71	17.4	2070
2060 X	5-28-71	11.7	2190
2070 F	5-28-71	11.8	2170
2080 F	5-28-71	11.9	2190
2090 X	5-28-71	11.8	2190
2100 X	5-28-71	12.3	2210
2110 F	6-03-71	14.6	2160
2120 F	6-03-71	14.3	2190
2130 F	6-03-71	13.0	2210
2121 F	6-04-71	12.6	2200
2140 F	6-04-71	12.1	2180
4051 X	6-07-71	16.7	2070
4061 F	6-07-71	16.4	2120
4071 X	6-08-71	19.9	2110
4081 F	6-09-71	14.0	2140
4101 X	6-09-71	15.3	2150
4031 X	6-10-71	14.9	2170
4041 X	6-10-71	15.4	2140
4091 X	6-10-71	15.2	2160
4011 X	6-11-71	15.1	2120
4121 X	6-11-71	15.8	2030
4021 X	6-11-71	15.1	2110
4111 X	6-11-71	16.1	2140
4131 X	6-15-71	13.5	2120
4141 X	6-15-71	11.1	2180

Notes:
1. "As Fired"
2. Softening temperature and reducing atmosphere
3. Only tests for which data is available are listed
4. No ash fusions were run on Series 5000

Table 11

SUMMARY SHEET
PROXIMATE COAL ANALYSES

Optimization Tests

		Proximate Analysis (Approx. 100%)				Determined Separately (Dry Basis)		
Test No.	Test Date	% Moisture	% Volatile Matter	% Fixed Carbon	% Ash	% Sulfur	% N_2	% O_2
1011 F	4-12-71	-	-	-	-	4.6	-	-
1012 F	4-12-71	-	-	-	-	4.2	-	-
1013 X	4-13-71	-	-	-	-	1.8	-	-
1021 F	4-13-71	9.7	31.3	45.2	13.8	2.4	1.4	8.2
1023 X	4-14-71	-	-	-	-	1.7	-	-
1031 F	4-13-71	-	-	-	-	2.3	-	-
1032 X	4-15-71	10.8	30.9	45.1	13.2	1.7	1.5	8.1
1041 F	4-16-71	-	-	-	-	1.6	-	-
1042 X	4-28-71	-	-	-	-	2.3	-	-
1051 X	4-16-71	-	-	-	-	1.6	-	-
1062 X	4-22-71	-	-	-	-	1.8	-	-
1072 X	4-22-71	-	-	-	-	2.1	-	-
1082 X	5-07-71	-	-	-	-	2.8	-	-
1092 X	4-22-71	9.5	31.6	44.0	14.9	2.5	1.5	7.2
1102 X	5-10-71	10.2	33.6	42.6	13.6	3.6	1.5	7.2
1113 X	5-11-71	-	-	-	-	2.0	-	-
1121 X	4-28-71	9.6	32.5	44.8	13.0	2.3	1.6	7.6
1131 X	4-29-71	-	-	-	-	1.8	-	-
1141 X	4-29-71	-	-	-	-	1.9	-	-
1152 X	5-10-71	-	-	-	-	3.6	-	-
1161 X	5-04-71	-	-	-	-	2.0	-	-
1171 X	5-05-71	-	-	-	-	2.6	-	-
1181 X	5-05-71	-	-	-	-	2.1	-	-
1192 X	5-16-71	-	-	-	-	3.1	-	-
1201 X	5-17-71	-	-	-	-	2.9	-	-
3021 X	5-24-71	-	-	-	-	2.8	-	-
3041 X	5-24-71	-	-	-	-	2.6	-	-
3011 F	5-24-71	3.2	34.4	42.5	19.9	3.8	1.4	7.2
3012 X	5-26-71	-	-	-	-	2.6	-	-
3031 X	5-26-71	-	-	-	-	2.5	-	-
3022 F	5-26-71	11.8	32.5	41.9	13.8	2.9	1.5	7.8
3051 X	5-25-71	-	-	-	-	2.0	-	-
3071 X	5-25-71	-	-	-	-	1.9	-	-

Table 11 (continued)

Proximate Coal Analyses

		Proximate Analysis (Approx. 100%)				Determined Separately (Dry Basis)		
Test No.	Test Date	% Moisture	% Volatile Matter	% Fixed Carbon	% Ash	% Sulfur	% N_2	% O_2
3061 X	5-25-71	11.4	30.6	43.8	14.3	2.2	1.6	-
3081 F	5-25-71	-	-	-	-	1.9	-	-
3091 X	5-27-71	-	-	-	-	2.6	-	-
3111 F	5-27-71	-	-	-	-	3.4	-	-
3101 X	5-27-71	-	-	-	-	3.3	-	-
3121 X	5-27-71	11.6	32.5	38.6	17.2	4.0	1.5	8.2
2010 X	5-20-71	-	-	-	-	3.5	-	-
2020 X	5-20-71	-	-	-	-	1.4	-	-
2030 X	5-21-71	-	-	-	-	2.7	-	-
2040 X	5-21-71	10.1	32.0	43.9	14.0	3.0	1.5	7.9
2050 X	5-21-71	-	-	-	-	3.1	-	-
2110 F	6-03-71	-	-	-	-	2.0	-	-
2120 F	6-03-71	-	-	-	-	1.4	-	-
2130 F	6-03-71	10.3	30.5	46.0	13.2	1.5	1.5	8.4
2121 F	6-04-71	-	-	-	-	1.5	-	-
2140 F	6-04-71	-	-	-	-	1.3	-	-
2060 X	5-28-71	-	-	-	-	1.7	-	-
2070 F	5-28-71	-	-	-	-	1.6	-	-
2080 F	5-28-71	-	-	-	-	1.7	-	-
2090 X	5-28-71	10.6	31.3	46.5	11.6	1.7	1.5	8.5
2100 X	5-28-71	-	-	-	-	1.6	-	-
4051 X	6-07-71	-	-	-	-	3.4	-	-
4061 F	6-07-71	10.6	31.1	42.1	16.2	3.3	1.4	7.6
4071 X	6-08-71	-	-	-	-	3.8	-	-
4081 F	6-09-71	-	-	-	-	2.2	-	-
4091 X	6-10-71	-	-	-	-	2.6	-	-
4101 X	6-09-71	-	-	-	-	2.4	-	-
4031 X	6-10-71	-	-	-	-	2.4	-	-
4041 X	6-10-71	-	-	-	-	2.5	-	-
4011 X	6-11-71	-	-	-	-	2.8	-	-
4121 X	6-11-71	9.8	31.7	42.7	15.8	3.8	1.4	7.4
4021 X	6-11-71	-	-	-	-	3.1	-	-
4111 X	6-11-71	-	-	-	-	2.9	-	-

FIGURE 65

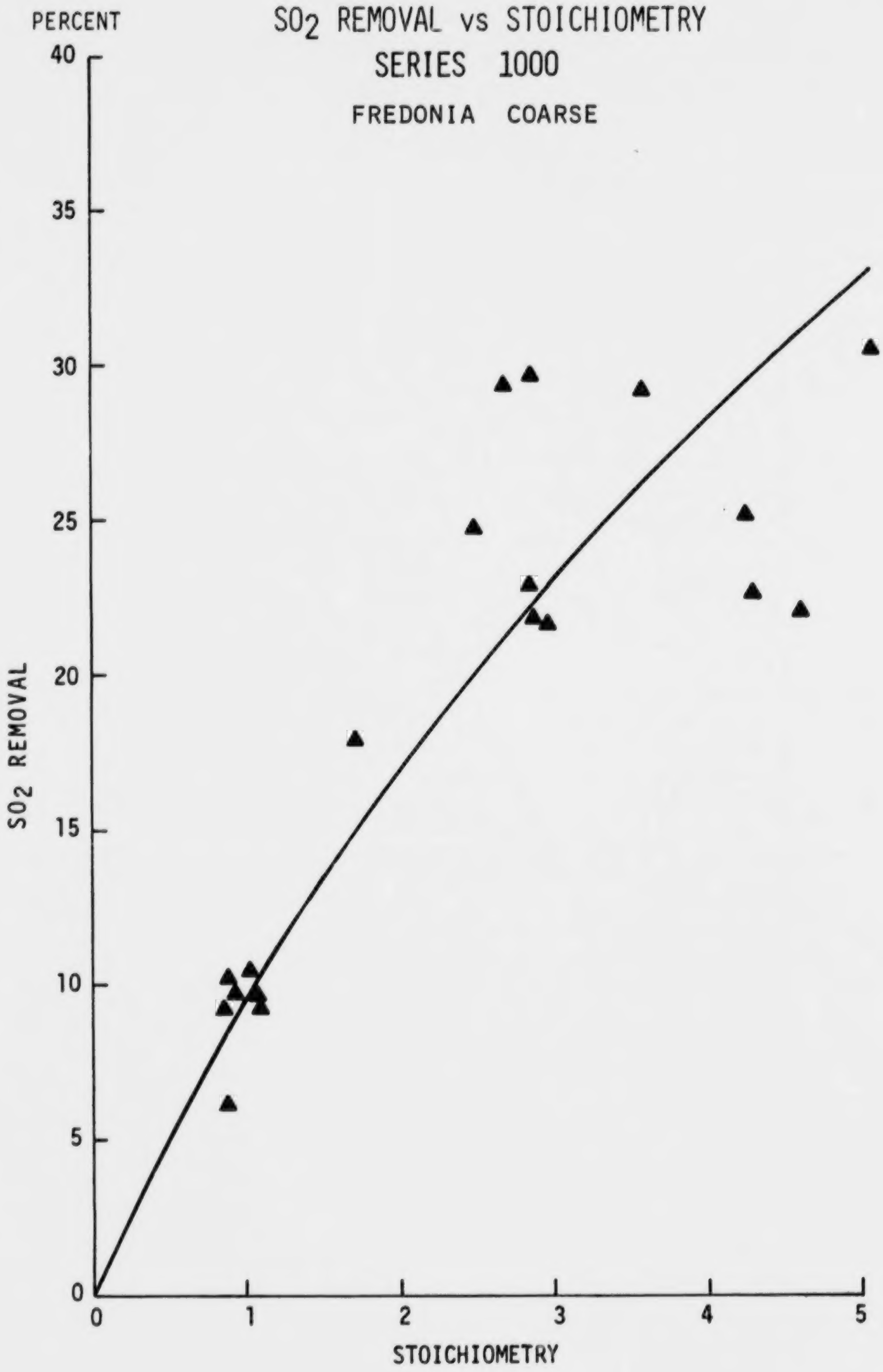

PERCENT
SO$_2$ REMOVAL vs STOICHIOMETRY
SERIES 1000
FREDONIA COARSE
40
35
30
25
20
15
10
5
0
SO$_2$ REMOVAL
0
1
2
3
4
5
STOICHIOMETRY

FIGURE 66

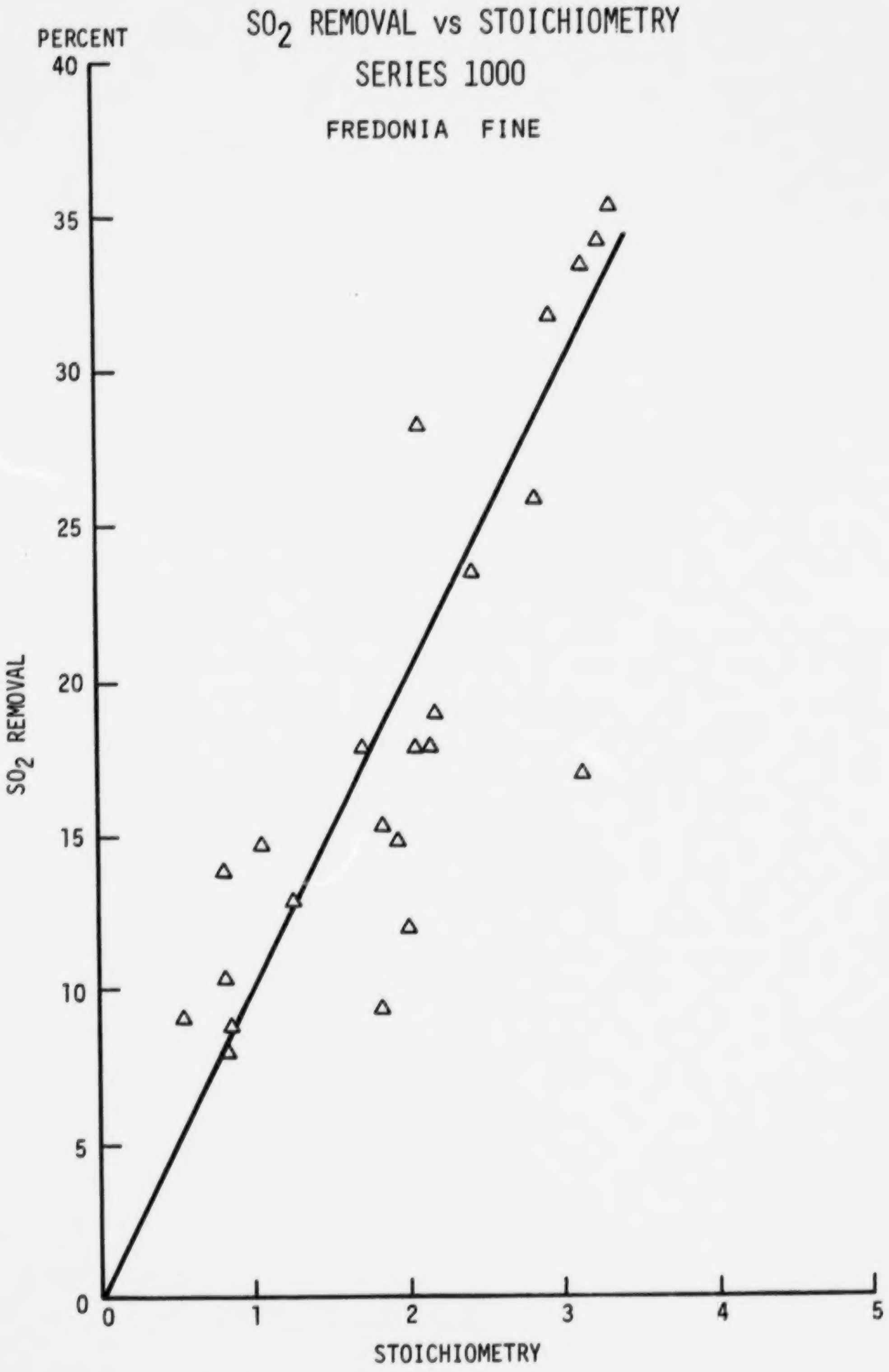
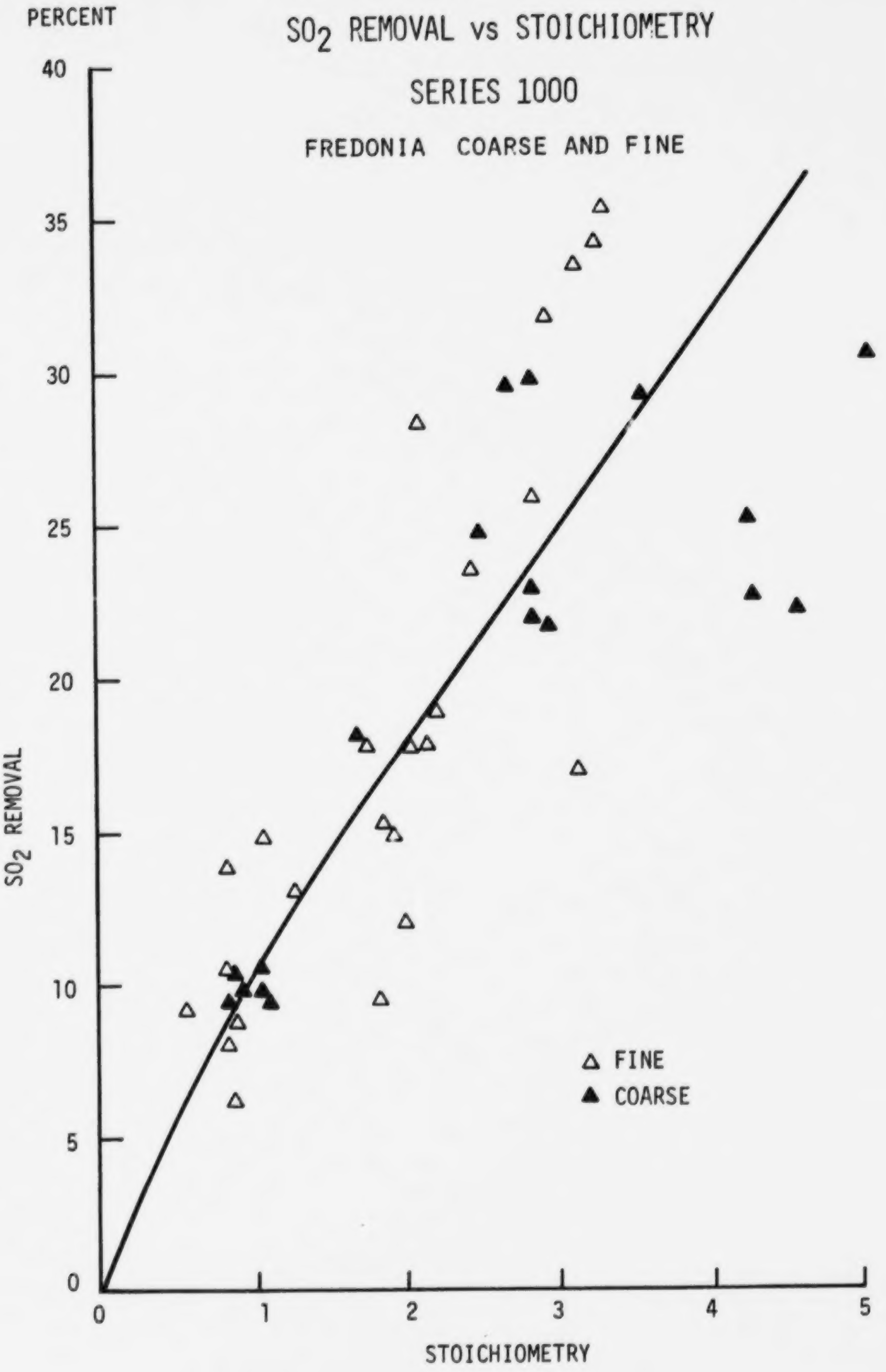

SO_2 REMOVAL vs STOICHIOMETRY
SERIES 1000
FREDONIA FINE
PERCENT
SO_2 REMOVAL
40
35
30
25
20
15
10
5
0
0
1
2
3
4
5
STOICHIOMETRY

FIGURE 67

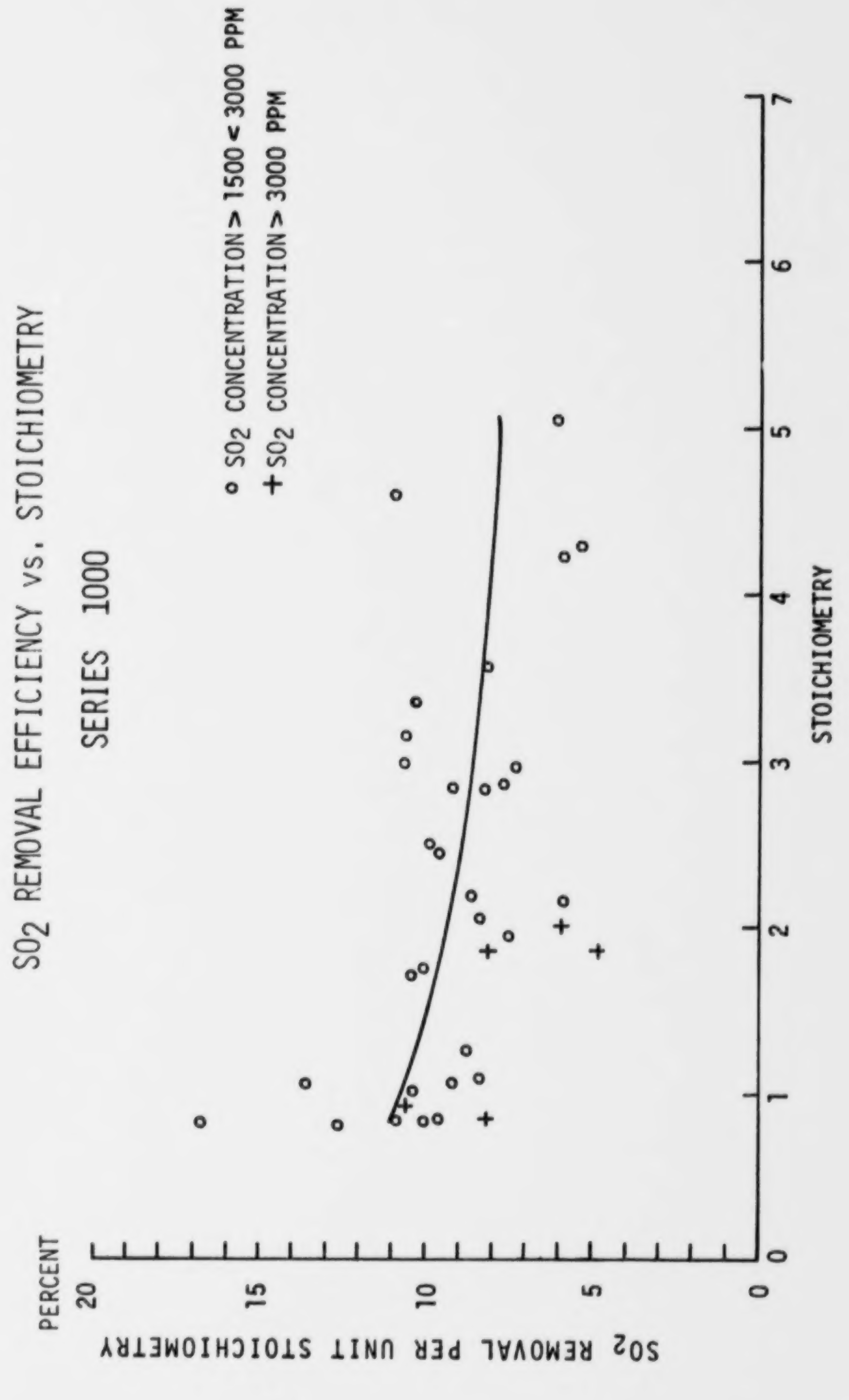


SO$_2$ REMOVAL vs STOICHIOMETRY

SERIES 1000

FREDONIA COARSE AND FINE

FIGURE 68



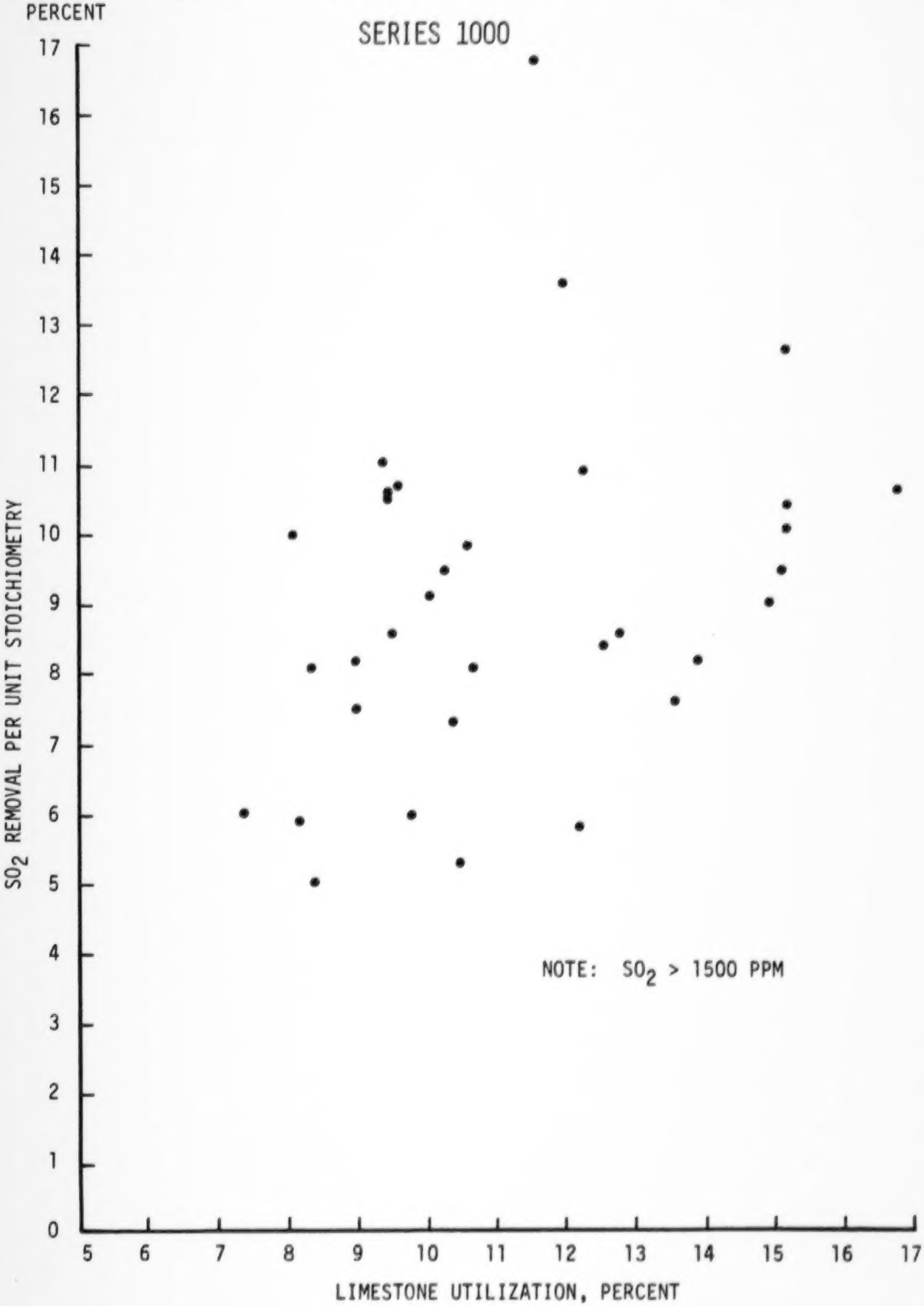
SO$_2$ REMOVAL EFFICIENCY vs. STOICHIOMETRY

SERIES 1000

FIGURE 69

SO_2 REMOVAL EFFICIENCY vs. LIMESTONE UTILIZATION

SERIES 1000



Series 2000

The limestone tested was Michigan marl (BCR 2129) which was identified in the bench scale tests as being a stone exhibiting high reactivity with SO_2. Since a limited tonnage of marl was available on site, the particle size was held constant (fine) and injection velocity at maximum. Boiler load was adjusted for full and half load tests. Injection nozzle angle was set at plus and minus 25°. Table 12 summarizes test parameters and results. Note that the -25° injection angle was repeated in the 5 half-load tests to benefit SO_2 removal by possible increase in particle residence time.

Figure 70 illustrates the important effect of boiler load over the broad range of stoichiometries tested. Half load (75 MW) SO_2 removal rate was 20% while full load (140 MW) was only 10% when injecting 1X stoichiometric. The figure also indicates the negative benefit of increasing stoichiometry and that it is more pronounced at lower boiler loads. The benefit to SO_2 removal of low load over full load is shown in figure 71 where % SO_2 removal per unit stoichiometry is plotted against stoichiometry. The trends are firm toward diminishing returns of high feed rates. Note in figure 72 that limestone utilizations did not exceed 20%.

From an operational standpoint the use of marl presented difficult raw material handling problems. The rail delivered marl contained 55% moisture which meant using a clam shell for unloading. A few tons were laboriously fed into the drier but only rolled up into balls about a quarter-inch in diameter and were not dry enough to attempt pulverization. The marl was then spread in windrows to air dry and after several rotations of these piles the marl was dry enough to successfully process through the dryer and ball mill.

Table 12

OPTIMIZATION TESTS
SUMMARY SHEET, SERIES 2000
Michigan Marl Full and Half Loads
(15 Tests)

Test No.	Test Date	Unit Load MW	Stoichiometry (1)	% Excess Air		Particle Size Index (1)	Injection Conditions			% SO_2 Removal		Initial SO_2 ppm		Limestone % Utilized	
				E	W		Angle Degrees (1)	Vel. F.P.S. (1)	Compressors (2)	E	W	E	W	E	W
2020X	5-20-71	141	2.78	24	22	2.6	-25°	72	2C + S	21.5	21.0	1280	1380	8.8	14.8
2010X	5-20-71	142	0.98	24	24	2.6	-25°	75	2C + S	6.3	7.9	2700	2680	9.2	11.3
2030X	5-21-71	141	1.08	22	24	2.5	-25°	83	2C + S	9.4	12.3	2440	2300	13.7	15.2
2040X	5-21-71	139	2.74	24	24	2.3	-25°	59	2C + S	21.3	25.2	2540	2280	9.7	13.0
2050X	5-21-71	140	0.80	20	28	2.3	-25°	82	2C + S	9.0	13.1	2280	2120	12.6	12.3
2060X	5-28-71	75	1.14	27	23	2.4	-25°	92	2C + S	17.6	23.3	1420	1540	19.6	19.6
2070F	5-28-71	75	3.57	33	31	2.4	-25°	80	2C + S	43.8	57.4	1460	1480	13.5	15.4
2080F	5-28-71	75	6.93	30	30	2.4	-25°	68	2C + S	62.6	75.5	1440	1280	10.7	11.3
2090X	5-28-71	75	1.07	33	30	2.6	-25°	92	2C + S	20.5	23.7	1320	1380	17.8	19.6
2100X	5-28-71	74	2.81	28	27	2.5	-25°	83	2C + S	41.5	51.5	1340	1400	16.7	18.5
2110F	6-03-71	140	0.88	24	23	2.2	+25°	86	2C + S	11.1	11.9	2060	2040	17.6	19.6
2120F	6-03-71	141	1.85	23	24	2.4	+25°	80	2C + S	19.4	21.2	1620	1500	11.3	12.8
2130F	6-03-71	140	3.46	25	23	2.4	+25°	72	2C + S	29.3	33.8	1480	1340	13.1	16.7
2140F	6-04-71	142	4.88	24	25	2.5	+25°	62	2C + S	31.5	41.4	1440	1280	8.2	9.7
2121F	6-04-71	140	2.41	24	24	2.4	+25°	73	2C + S	25.6	27.6	1460	1440	11.9	12.7

Notes: 1. Major independent variable
2. Two compressors plus boost steam

FIGURE 70

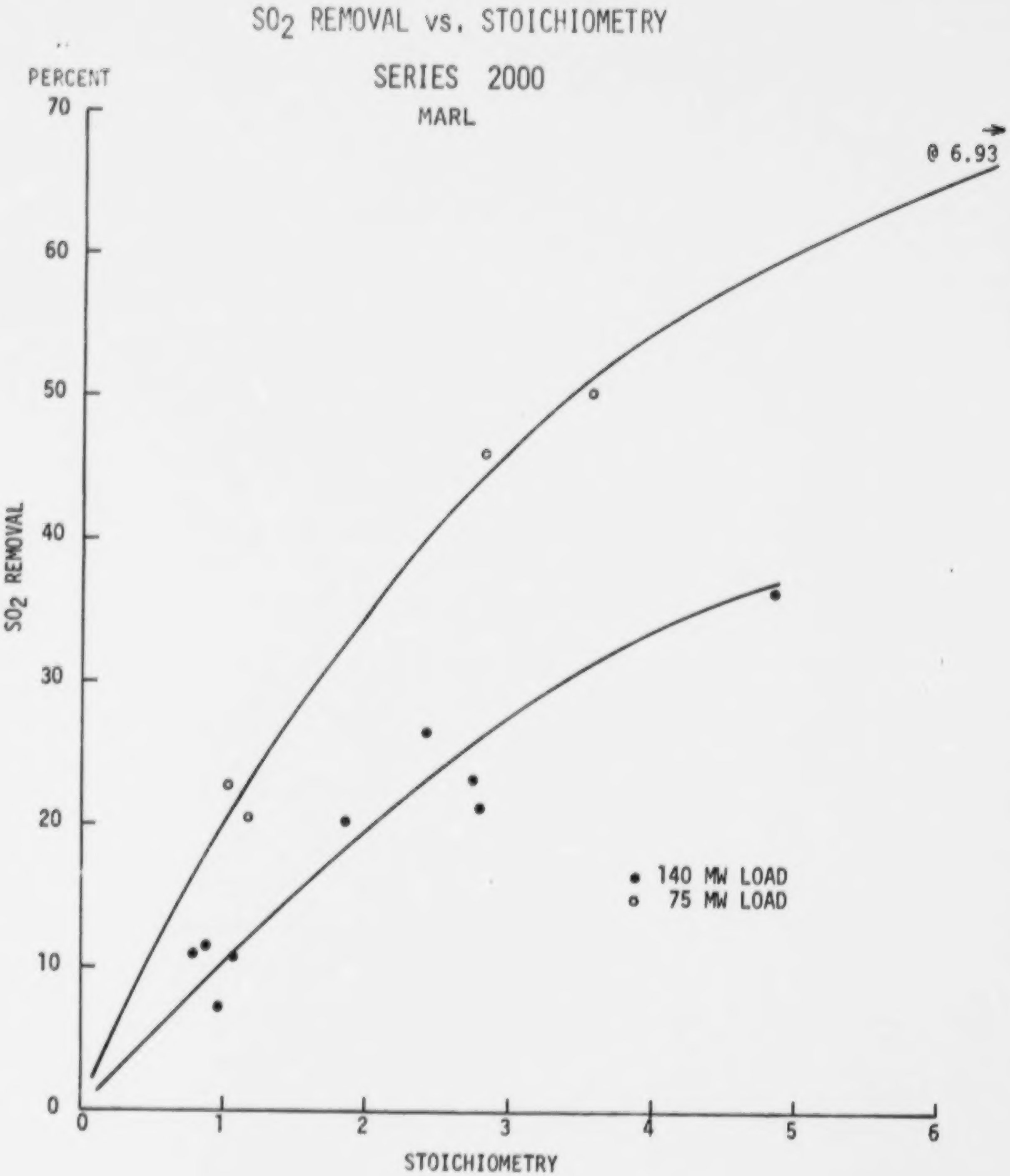
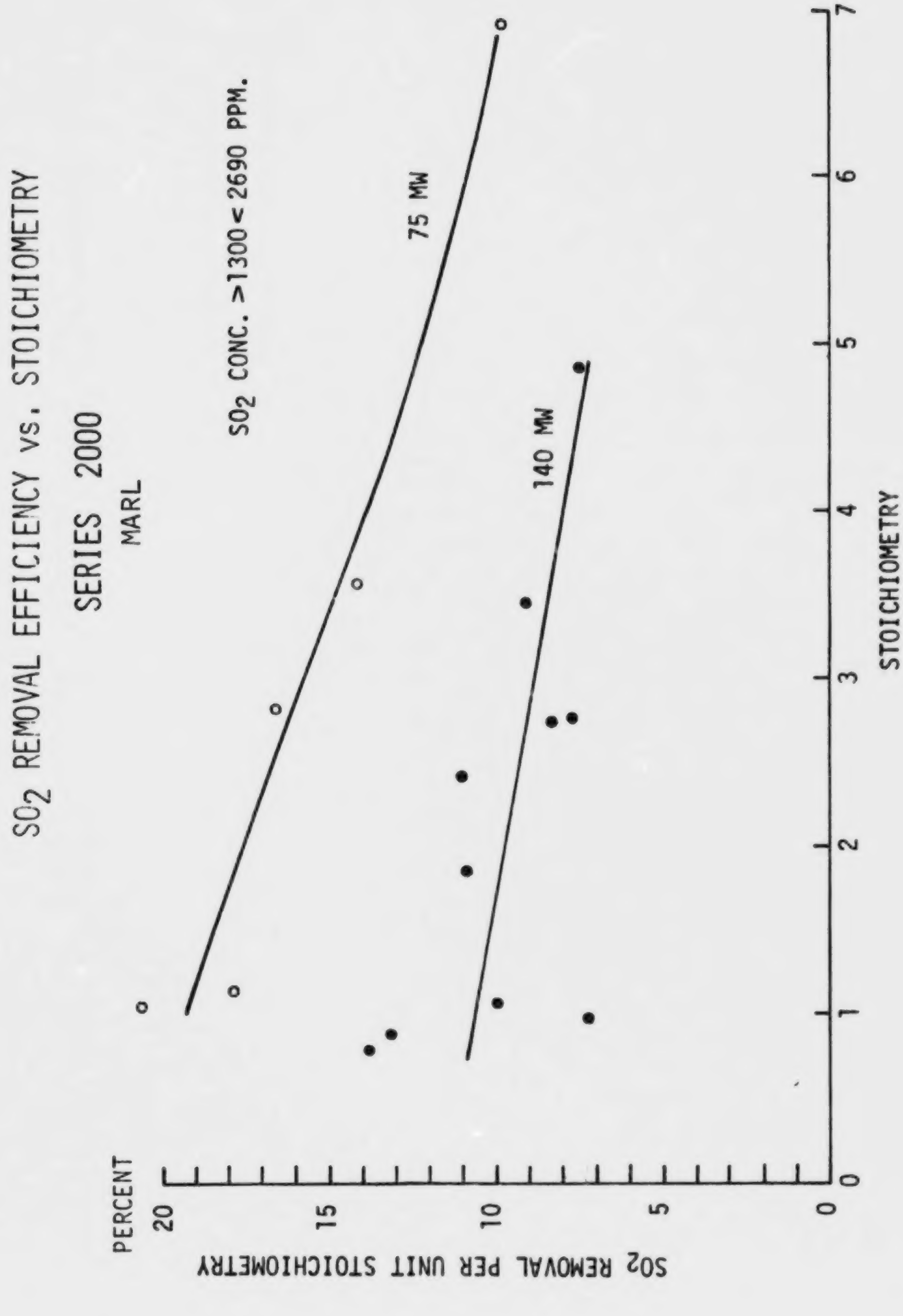

SO$_2$ REMOVAL vs. STOICHIOMETRY
SERIES 2000
MARL
PERCENT
SO$_2$ REMOVAL
70
60
50
40
30
20
10
0
0
1
2
3
4
5
6
STOICHIOMETRY
@ 6.93
● 140 MW LOAD
○ 75 MW LOAD

FIGURE 71



SO$_2$ REMOVAL EFFICIENCY vs. STOICHIOMETRY

SERIES 2000

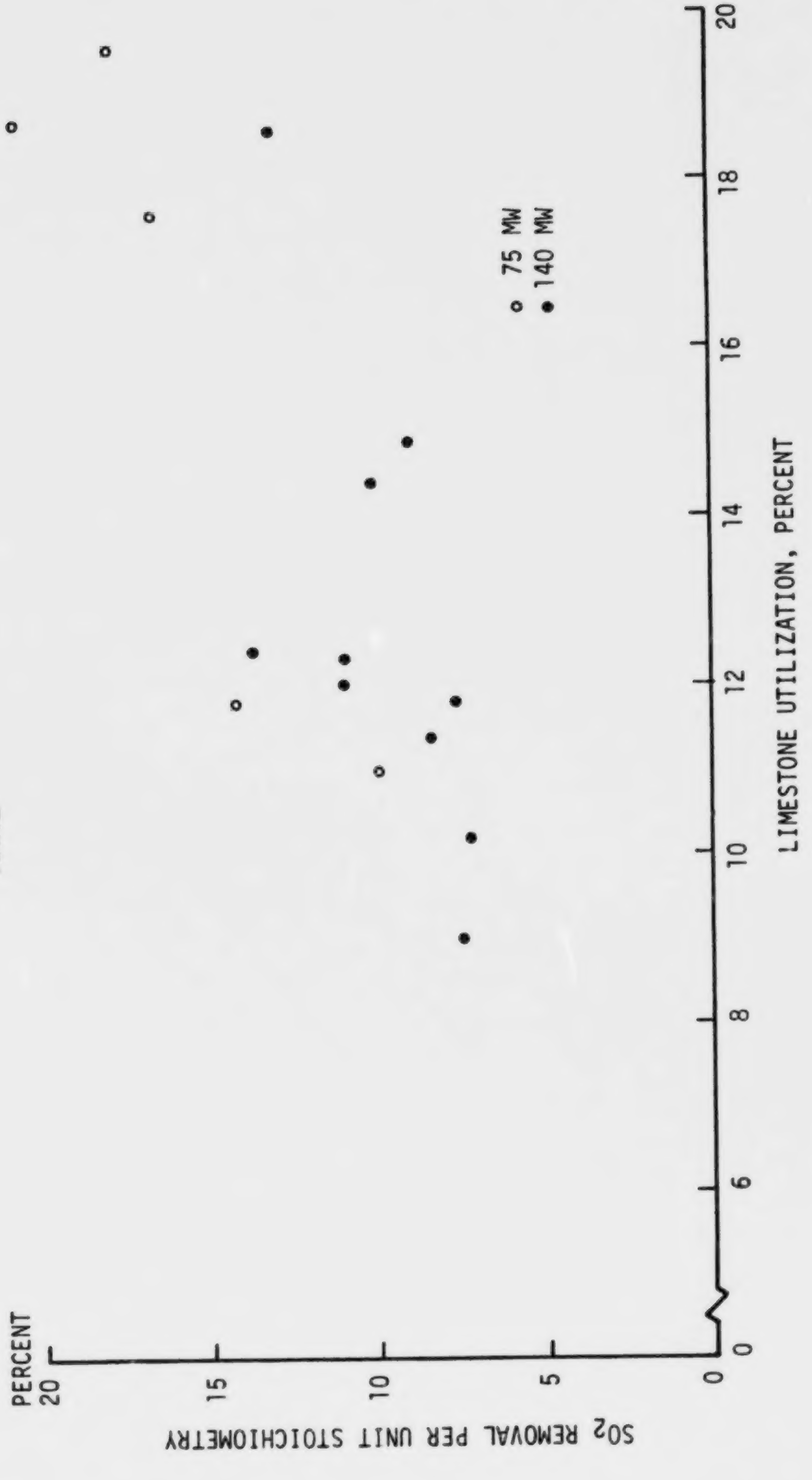
MARL

FIGURE 72

SO$_2$ REMOVAL EFFICIENCY vs. LIMESTONE UTILIZATION

SERIES 2000

MARL



Series 3000

This group of 14 tests was conducted for the purpose of time-temperature sensitivity measurements at low load for comparison with series 1000 data. Unit 10 was held at nominal 75-MW load and Fredonia limestone of fine particle size (avg. 3.2 size index) was injected at both 0° and -25° angles. Tables 13 is a summary sheet for the series 3000 tests. Figure 73 is a plot of % SO_2 removal vs. stoichiometry in which data points for the various burner combinations are identified. The data indicates no discernible difference in SO_2 removal resulting from use of either upper 8 burners or lower 8 burners.

These low load tests at 75-MW show that fine grind Fredonia limestone removed about 15% of the SO_2 at 1X stoichiometric and 28% at 2X stoichiometric. Results at higher injection rates show greater removals but with greater spread between east and west halves of the furnace. Removals were based on UV analyzer readings of SO_2 concentration and crossed in-put checks were often made on these two analyzers to verify that the readings represented the respective SO_2 concentrations in each furnace. It was assumed that limestone input to each furnace was equalized by the distributor.

As shown in figure 74, at low load there was a steady reduction in % SO_2 removal per unit stoichiometry as feed rate was increased to 4X stoichiometric. Note that SO_2 concentration ranged only 770 ppm during these tests.

The average limestone utilization for Series 3000 was 15% as compared with 11% for Series 1000, thus, low load resulted in a 36% improvement in utilization over the full load condition.

Figure 75 is a plot of % SO_2 removal efficiency vs. % limestone utilizations. Having completed both full load tests (Series 1000) and half load tests (Series 3000) it is possible to see load effects on % SO_2 removal, as shown in figure 76. Half load SO_2 removals were 50% better than full load removals at 1X stoichiometric.

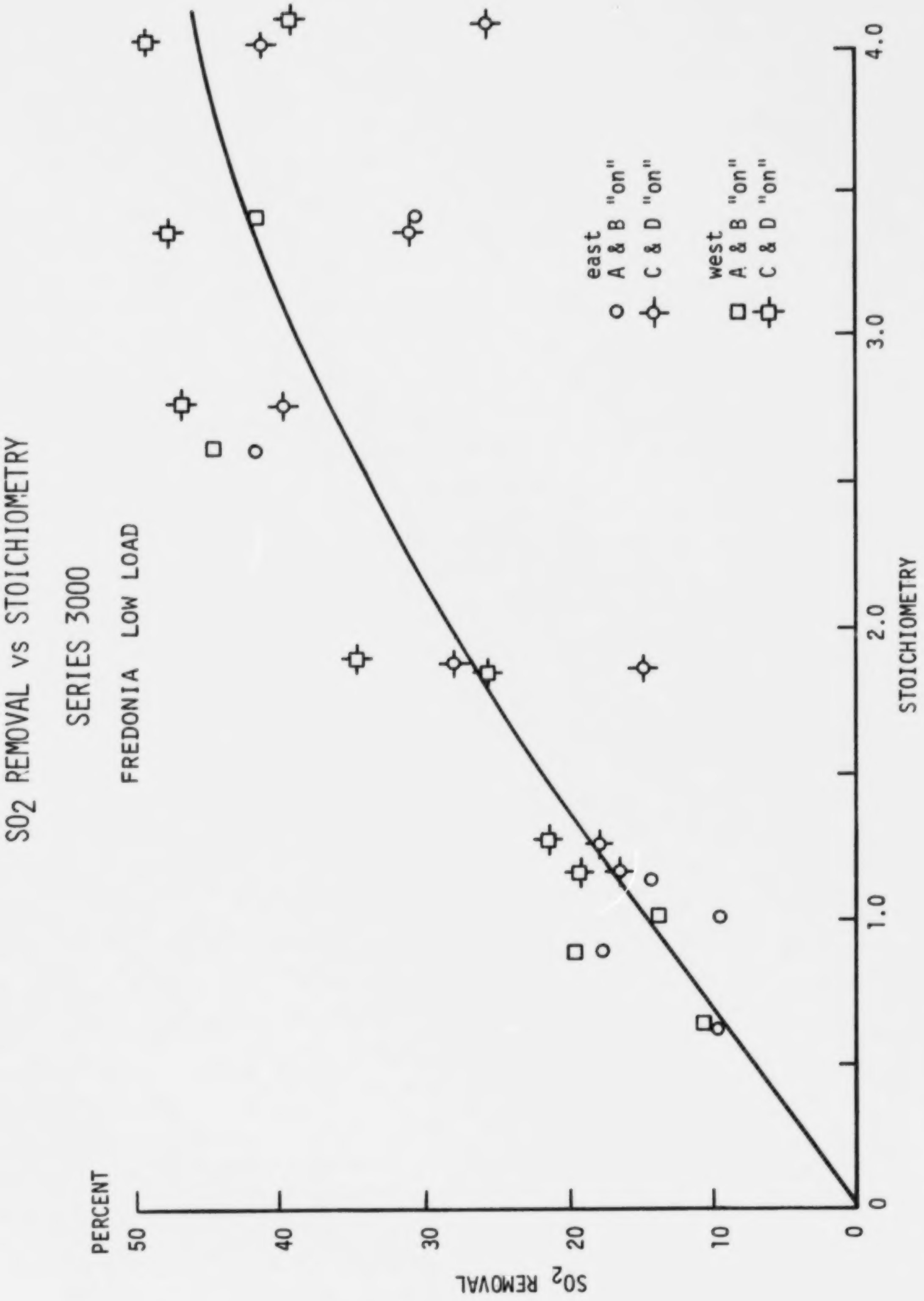
Table 13

OPTIMIZATION TESTS
SUMMARY SHEET, SERIES 3000
Fredonia Low Load
(14 Tests)

Test No.	Test Date	Unit Load MW	Stoich-iometry*	% Excess Air		Particle Size Index*	Injection Conditions			% SO_2 Removal		Initial SO_2 ppm		Limestone % Utilized	
				E	W		Angle Degrees*	Vel. F.P.S.*	Com-pressors	E	W	E	W	E	W
3021X	5-24-71	73	1.15	31	29	2.6	-25°	92	2C + S	14.1	19.7	2480	2580	16.8	15.8
3041X	5-24-71	74	3.41	29	32	3.9	-25°	60	2C + S	30.3	41.5	2540	2620	15.1	12.9
3011X	5-24-71	75	1.01	29	29	3.5	0°	86	2C	9.4	13.8	2580	2760	17.3	15.9
3051X	5-25-71	75	1.16	30	20	2.9	-25°	90	2C + S	16.6	19.2	2160	2260	18.8	16.4
3071X	5-25-71	75	2.79	29	31	2.9	-25°	66	2C + S	39.5	46.5	2100	2080	15.1	15.1
3061X	5-25-71	75	1.27	33	32	3.5	0°	91	2C + S	17.9	21.7	1920	1960	16.0	14.4
3081X	5-25-71	75	4.04	32	33	3.5	0°	67	2C + S	41.0	49.0	1880	1920	13.2	10.6
3012F	5-26-71	75	0.89	34	27	2.7	0°	90	2C + S	17.6	19.3	1940	2120	13.9	16.5
3031F	5-26-71	75	2.63	37	32	3.9	0°	72	2C + S	41.6	44.4	2240	2340	11.6	13.5
3022F	5-26-71	75	0.63	32	33	2.2	-25°	92	2C + S	9.3	10.6	2220	2400	18.5	19.1
3091X	5-27-71	75	1.90	22	30	2.5	-25°	75	2C + S	27.8	34.5	2180	2200	15.5	17.2
3111F	5-27-71	74	3.37	16	29	2.4	-25°	55	2C + S	30.9	47.1	2480	2420	9.8	15.0
3101X	5-27-71	74	1.86	20	33	5.5	0°	75	2C + S	14.6	26.3	2740	2540	14.4	15.0
3121X	5-27-71	74	4.10	18	27	3.1	0°	44	2C + S	25.5	39.0	2660	2540	11.8	13.4

Notes: *Major independent variable

FIGURE 73



SO$_2$ REMOVAL vs STOICHIOMETRY

SERIES 3000

FREDONIA LOW LOAD

FIGURE 74

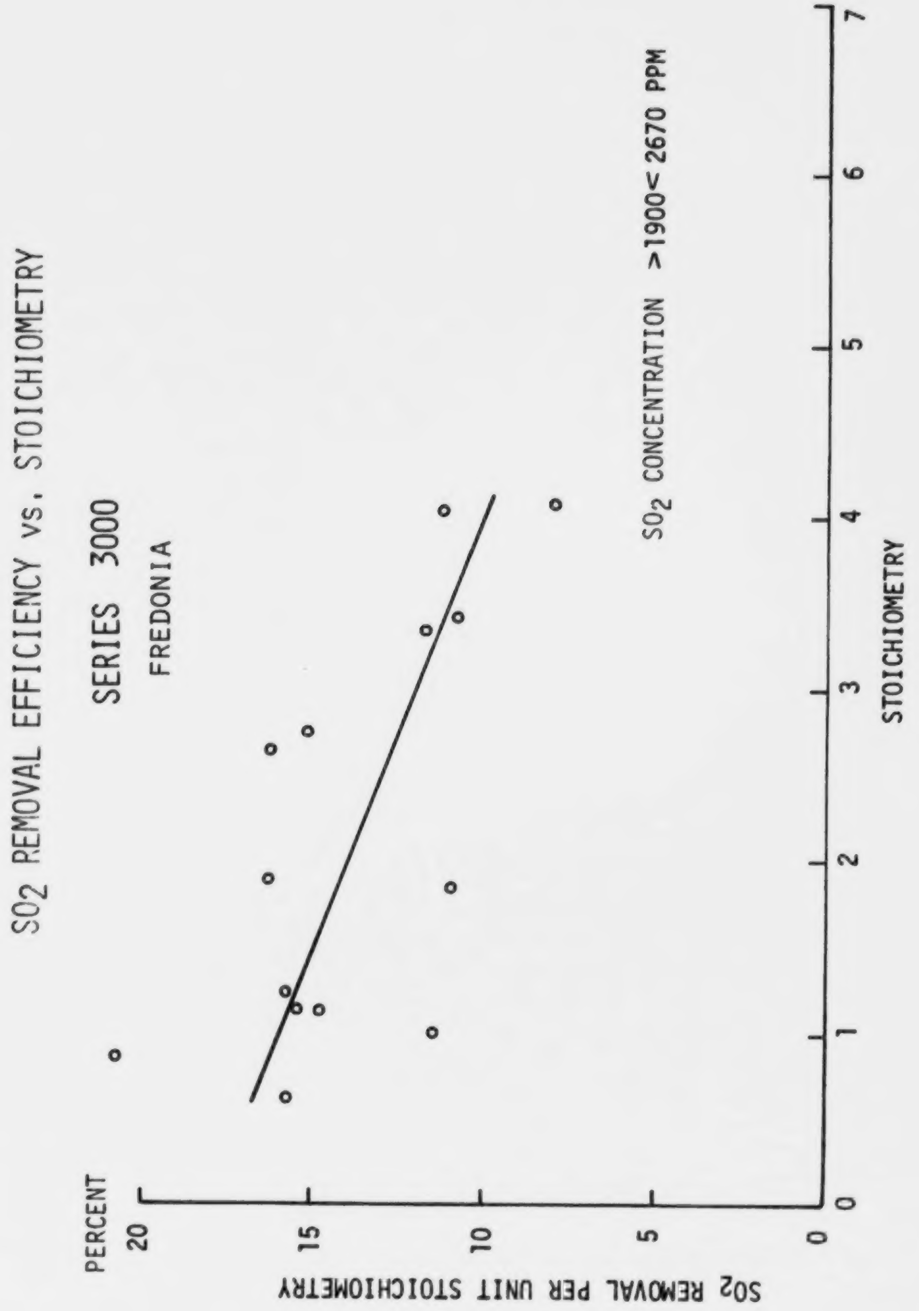
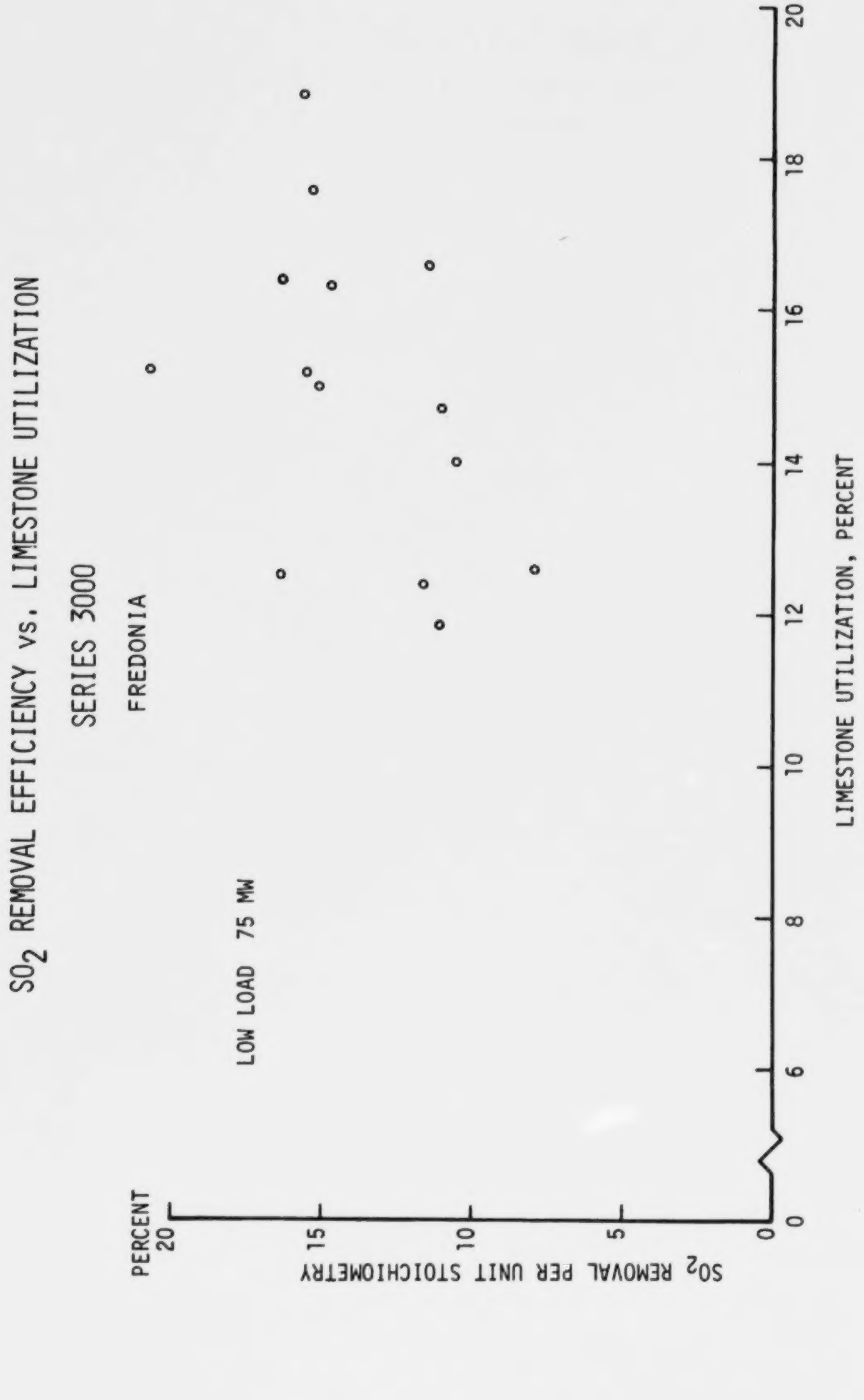

SO_2 REMOVAL EFFICIENCY vs. STOICHIOMETRY
SERIES 3000
FREDONIA
SO_2 CONCENTRATION >1900< 2670 PPM
PERCENT
SO_2 REMOVAL PER UNIT STOICHIOMETRY
20
15
10
5
0
STOICHIOMETRY
0
1
2
3
4
5
6
7

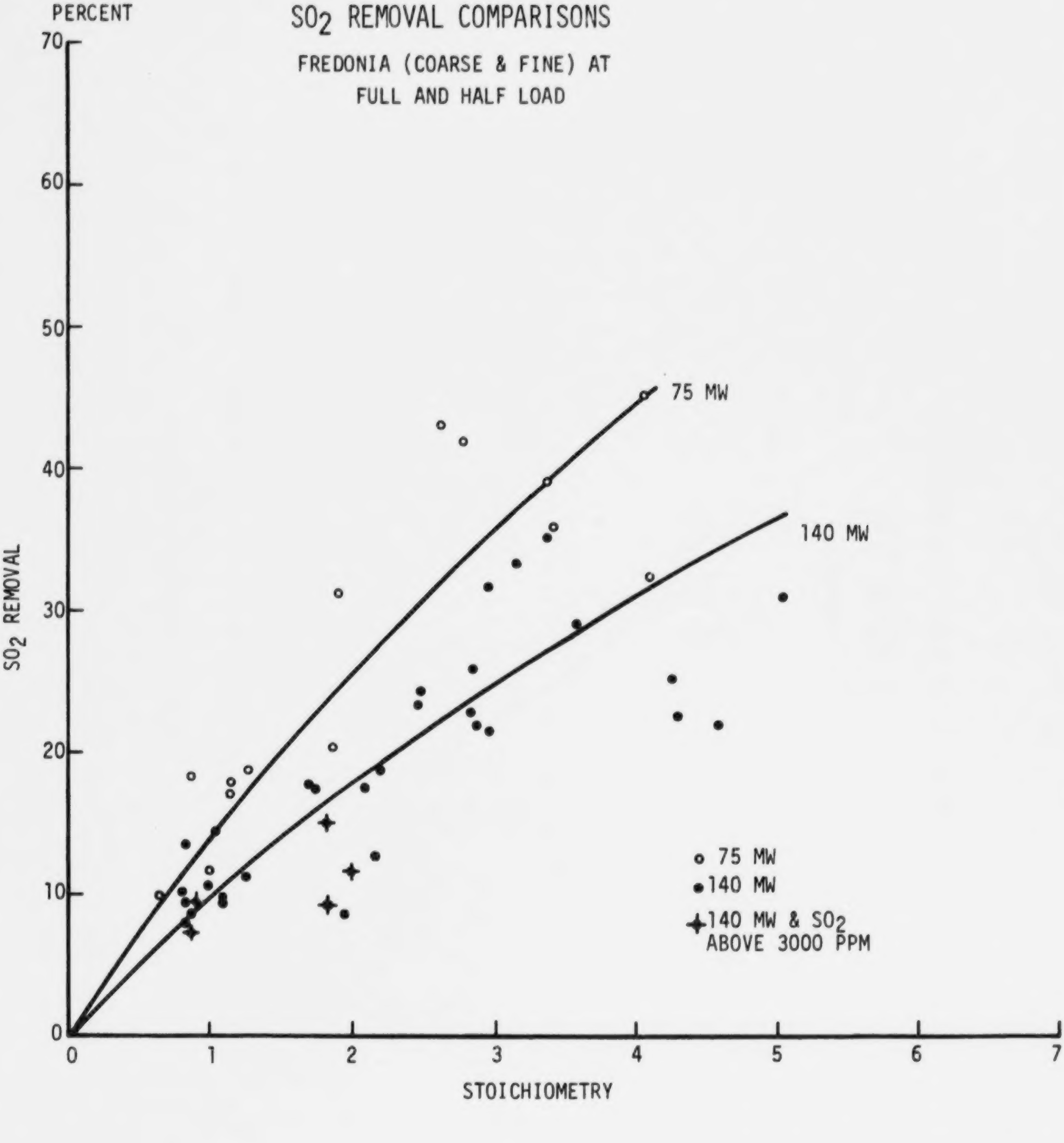
FIGURE 75



SO$_2$ REMOVAL EFFICIENCY vs. LIMESTONE UTILIZATION

SERIES 3000

FREDONIA


PERCENT
SO$_2$ REMOVAL COMPARISONS
FREDONIA (COARSE & FINE) AT
FULL AND HALF LOAD
70
60
50
40
30
20
10
0
SO$_2$ REMOVAL
75 MW
140 MW
○ 75 MW
● 140 MW
✦ 140 MW & SO$_2$ ABOVE 3000 PPM
0
1
2
3
4
5
6
7
STOICHIOMETRY

Series 4000

Aragonite (BCR 2208) was the third type of limestone evaluated in the Shawnee full-scale tests. Only 200 tons were available for full load (140 MW) and half load (75 MW) tests. Another controlled variable was particle size. Coarse and fine stone was injected at the plane A-A. Except for two full load tests with frontal injection (O° angle), all tests were at -25° angle to increase residence time. For the 75 MW tests only the lower two burner rows, C and D, or 8 burners were operated. This move would provide the least severe injection conditions as regards possibilities of particle deadburning. The A and B rows were off and their secondary air dampers closed.

Summary results for the Series 4000 tests are shown in table 14.

The SO_2 removal rates for all 17 tests run on aragonite are shown in figure 77 where removals for each half of the furnace are plotted separately. Note the four test points for test 4131 and 4141 where front injection was used. Only 6 tests were run at half load and the data scatter is shown in figure 78, where % SO_2 removal per unit stoichiometry is plotted against stoichiometry. In this case, low load appears to have produced less good removal than full load.

Limestone utilization for Series 4000 is plotted in figure 79 and ranged from 9.6% to 16.3%; data for the 75 MW runs being only a few percentage points better than at 140 MW load.

Particle size index (by Fisher sizer measurement) ranged from 4 to nearly 14. The SO_2 removal efficiency plotted against particle size is shown in figure 80. Little effect of particle size, per se, on SO_2 removal was detected in this series.

Table 14

OPTIMIZATION TESTS
SUMMARY SHEET, SERIES 4000
Aragonite - Full and Half Loads
(17 Tests)

Test No.	Test Date	Unit Load MW	Stoich-iometry	% Excess Air		Particle Size Index	Injection Conditions			% SO_2 Removal		Initial SO ppm		Limestone % Utilized	
				E	W		Angle Degrees	Vel. F.P.S.	Com-pressors	E	W	E	W	E	W
4051X	6-07-71	140	1.06	23	23	4.3	-25°	71	2C + S	11.0	14.0	2920	2720	13.4	13.9
4061F	6-07-71	139	3.43	24	25	3.9	-25°	52	2C + S	18.0	34.0	2740	2560	12.0	13.4
4071X	6-08-71	141	1.03	25	24	13.7	-25°	64	2C + S	9.4	5.9	2980	3000	14.4	12.5
4081F	6-09-71	140	3.47	24	25	6.9	-25°	32	2C + S	19.4	22.2	2440	2420	11.4	10.1
4101X	6-09-71	140	1.04	30	31	11.3	-25°	76	2C + S	10.1	8.5	1960	2240	12.6	12.9
4031X	6-10-71	75	1.07	24	23	7.4	-25°	88	2C + S	8.6	7.8	2480	2500	14.8	16.6
4041X	6-10-71	75	2.89	23	24	7.4	-25°	67	2C + S	12.5	13.8	2450	2330	10.6	8.9
4091X	6-10-71	140	0.79	20	11	7.4	-25°	77	2C + S	5.7	4.8	2440	2800	12.7	15.1
4011X	6-11-71	75	0.77	24	25	4.6	-25°	89	2C + S	8.9	11.6	2440	2490	15.2	17.4
4121X	6-11-71	75	1.97	16	17	4.6	-25°	74	2C + S	21.8	21.8	2760	2760	15.4	15.9
4021X	6-11-71	75	2.78	25	23	5.1	-25°	68	2C + S	26.2	24.1	2580	2620	11.4	12.5
4111X	6-11-71	75	5.14	24	23	5.1	-25°	54	2C + S	35.3	33.7	2560	2680	9.4	9.9
*4131X	6-15-71	142	1.69	25	24	4.6	0°	69	2C + S	16.4	13.5	2180	2400		
*4141X	6-15-71	143	5.76	24	23	4.6	0°	41	2C + S	33.8	32.8	1900	2140		
4151X	6-23-71	140	1.38	27	22	4.5	-25°	77	2C + S	14.4	15.4	2190	2200		
4161X	6-24-71	141	2.04	24	23	4.7	-25°	79	2C + S	19.1	20.5	1940	2040		
4171X	6-25-71	141	1.24	24	24	4.7	-25°	84	2C + S	13.7	11.8	1880	2290		

*Front Injection

FIGURE 77

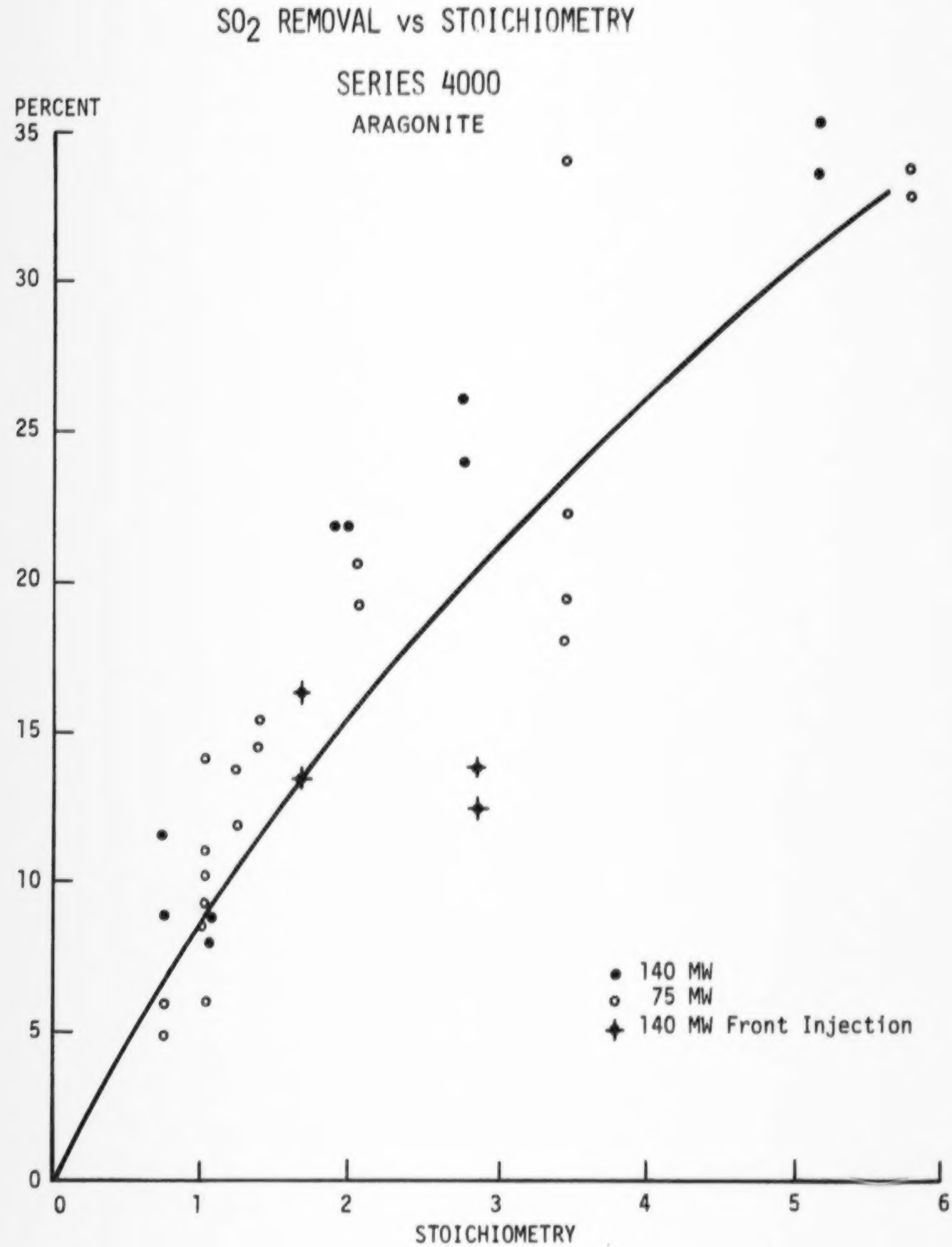

SO2 REMOVAL vs STOICHIOMETRY
SERIES 4000
ARAGONITE
PERCENT
35
30
25
20
15
10
5
0
0
1
2
3
4
5
6
STOICHIOMETRY
● 140 MW
o 75 MW
✦ 140 MW Front Injection

FIGURE 78

SO_2 REMOVAL EFFICIENCY vs. STOICHIOMETRY
AT FULL AND HALF LOADS

SERIES 4000

ARAGONITE

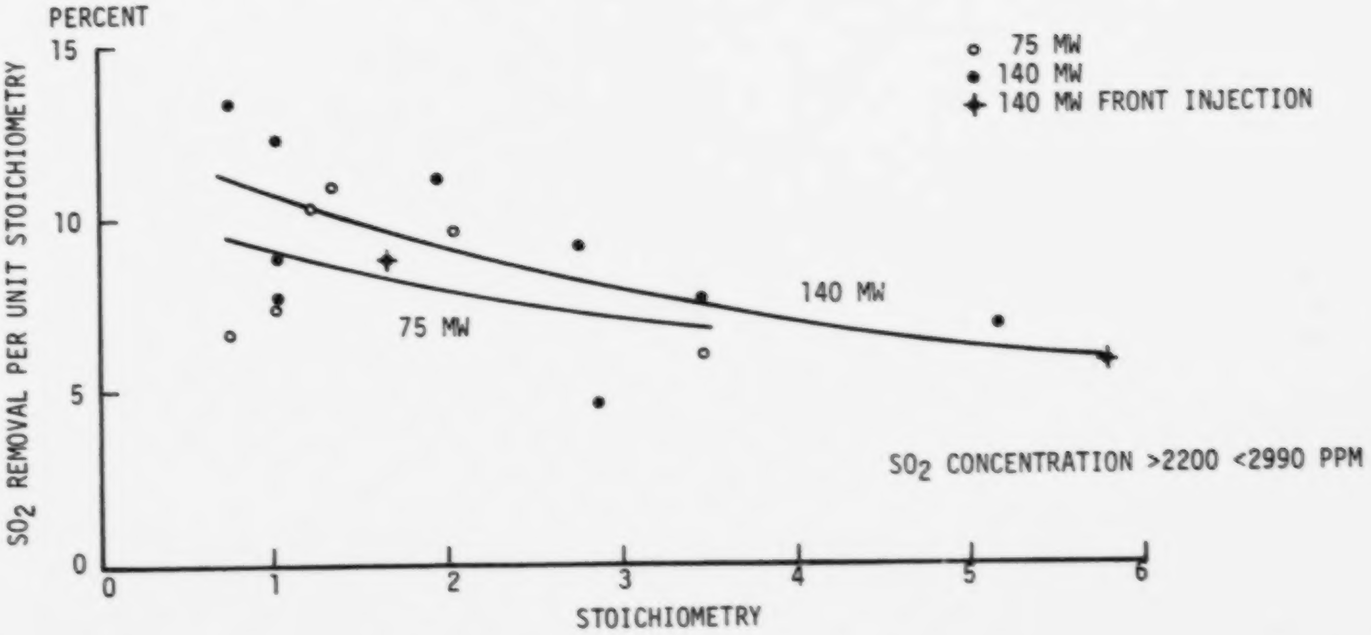


FIGURE 79

SO_2 REMOVAL EFFICIENCY vs. LIMESTONE UTILIZATION

SERIES 4000

ARAGONITE

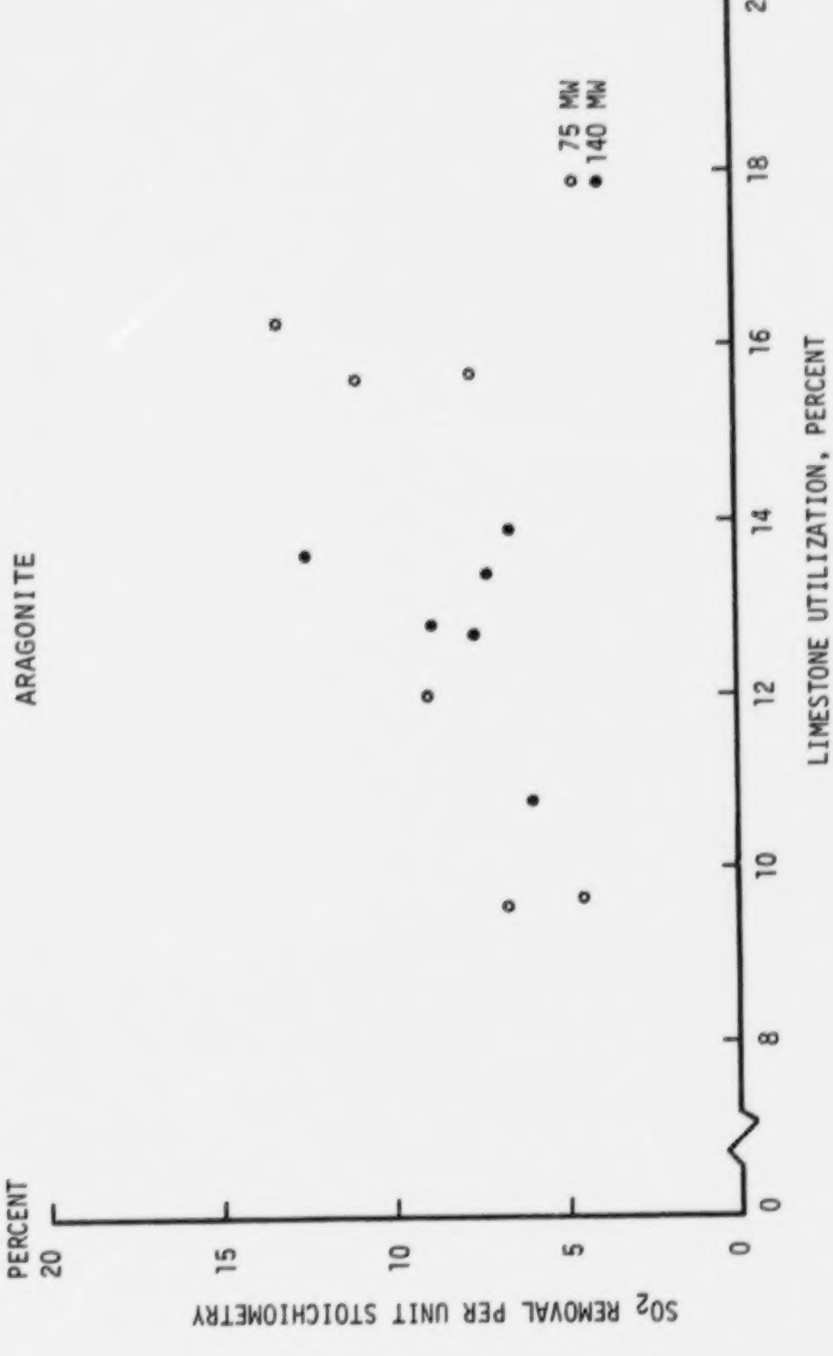
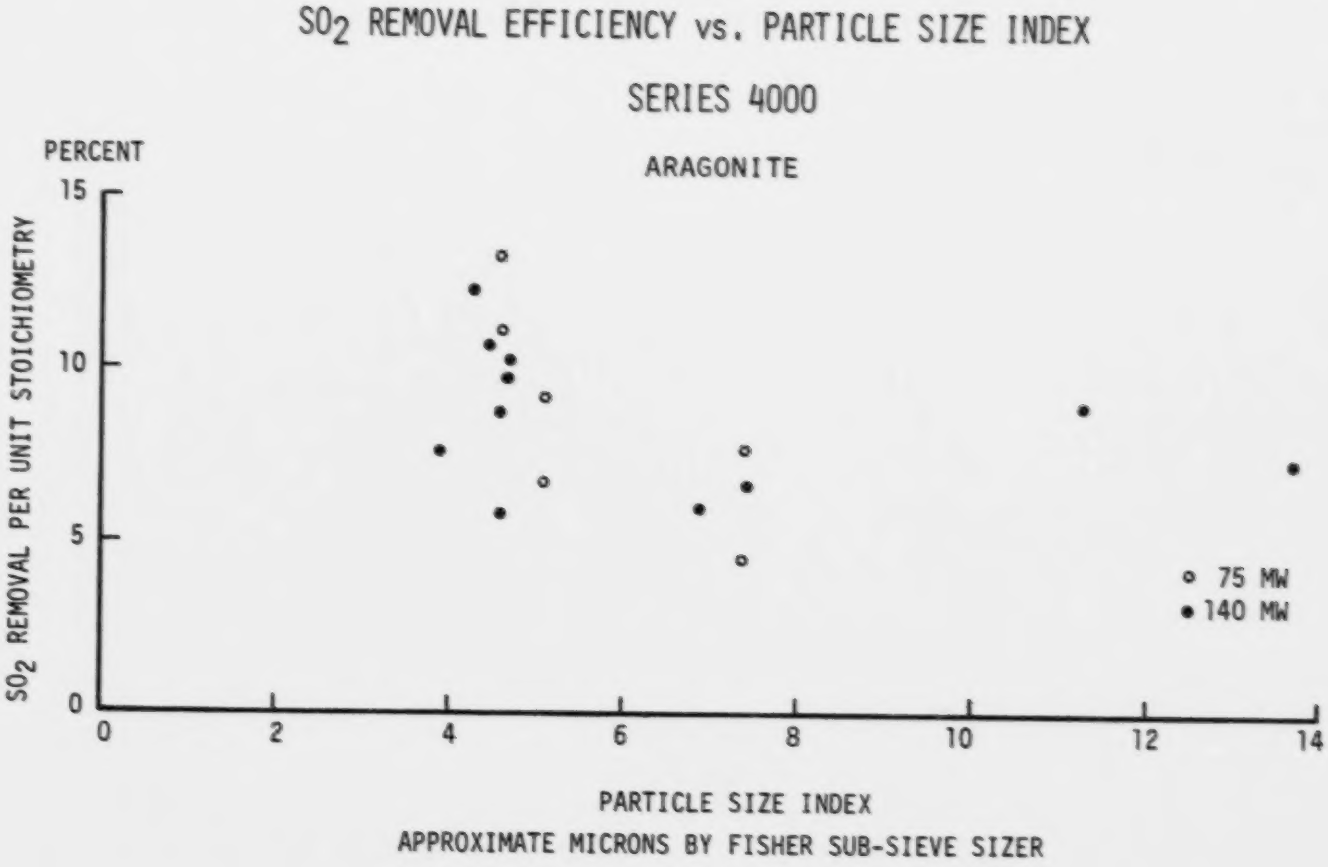


FIGURE 80



SO_2 REMOVAL EFFICIENCY vs. PARTICLE SIZE INDEX

SERIES 4000

ARAGONITE

Series 5000

The purpose of running this series was to determine SO_2 removal rates while burning coal with 0.8% or less total sulfur. This would extend the lower limit of initial SO_2 concentration data. Coal in the bunker was drawn down to minimum safe levels before bunkering this eastern Kentucky low sulfur coal for which sulfur averaged 0.76% and ranged from 0.65% to 0.87%. (A portion of this coal was reserved for use during precipitator evaluations by Cottrell Environmental Systems in July, see Appendix F, Limestone Injection Effects on Solids Collection System.)

Table 15 is the summary sheet for this series of 13 tests conducted on June 28 and 29, 1971.

Boiler load was to be held constant at 140 MW for this series but mechanical problems with a mill caused reduction to 3/4 load for 5 tests. Fredonia limestone was used and the fine particle size index averaged 2.7. Injection angle and operation of two air compressors were held constant for all tests but stoichiometries were generally higher than desired for this series.

The % SO_2 removal vs. stoichiometry for the Series 5000 tests is plotted in figure 81. They are based on averaged east and west furnace data and extrapolated below 1.6X stoichiometric.

Nearly 11% SO_2 removal was attained with 2X stoichiometric feed-rate using fine grind Fredonia limestone.

The benefit of load reduction shown in previous test series was repeated in this series. There appeared to be a slight improvement in SO_2 removal for test 5131 with a 1.75X stoichiometric, average removal of 11.4% at a load of 108 MW compared with test 5021 with a 1.61X stoichiometric and 9.0% removal at 133 MW. This SO_2 removal at reduced load is shown graphically in figure 82 where removal efficiency is plotted over nearly one order of magnitude of stoichiometry.

Sensitivity of SO_2 removal to the initial concentration of SO_2 in the gas is shown in figure 83 for this series. Figure 84 is a plot of SO_2 removal efficiency plotted against the % of limestone utilization for each test with low sulfur coal.

Table 15

OPTIMIZATION TESTS
SUMMARY SHEET, SERIES 5000
Low Sulfur Coal - Full to 3/4 Load
(13 Tests, Fredonia Limestone)

Test No.	Test Date	Unit Load MW	Stoich-iometry	% Excess Air E	% Excess Air W	Particle Size Index	Injection Conditions: Angle Degrees	Injection Conditions: Vel. F.P.S	Injection Conditions: Com-pressors	% SO_2 Removal E	% SO_2 Removal W	Initial SO_2 ppm E	Initial SO_2 ppm W	Limestone % Utilized E	Limestone % Utilized W
5011F	6-28-71	141	2.03	13	12	2.6	-25°	88	2C	8.4	10.1	1100	1040	10.5	14.1
5031X	6-28-71	141	6.71	11	12	2.6	-25°	84	2C	17.2	24.1	1050	940	5.4	5.3
5051X	6-28-71	140	9.57	10	11	2.8	-25°	46	2C	21.4	28.1	920	840	4.2	3.6
5071X	6-28-71	140	5.33	20	21	2.8	-25°	59	2C	16.8	23.6	840	890	5.9	3.5
5081X	6-28-71	140	5.52	19	18	2.7	-25°	59	2C	18.0	26.7	840	900	5.1	5.1
5021X	6-29-71	133	1.61	31	32	2.7	-25°	91	2C	9.1	8.9	900	1030	16.1	8.1
5041X	6-29-71	133	5.67	30	32	2.7	-25°	62	2C	26.3	29.6	840	990	5.8	5.5
5061X	6-29-71	133	8.93	29	33	2.7	-25°	42	2C	38.1	42.0	760	800	5.0	4.5
5091X	6-29-71	114	4.54	31	32	2.6	-25°	75	2C	24.8	33.7	840	740	6.9	5.2
5101X	6-29-71	112	8.91	33	33	2.6	-25°	60	2C	32.3	43.3	740	750	6.2	5.4
5131X	6-29-71	108	1.75	20	20	2.6	-25°	92	2C	11.7	11.1	830	960	8.8	7.1
5141X	6-29-71	108	4.35	21	24	2.6	-25°	75	2C	25.0	25.2	830	820	7.6	7.1
5151X	6-29-71	108	7.68	31	24	2.8	-25°	60	2C	35.8	37.4	810	870	5.1	5.3

FIGURE 81

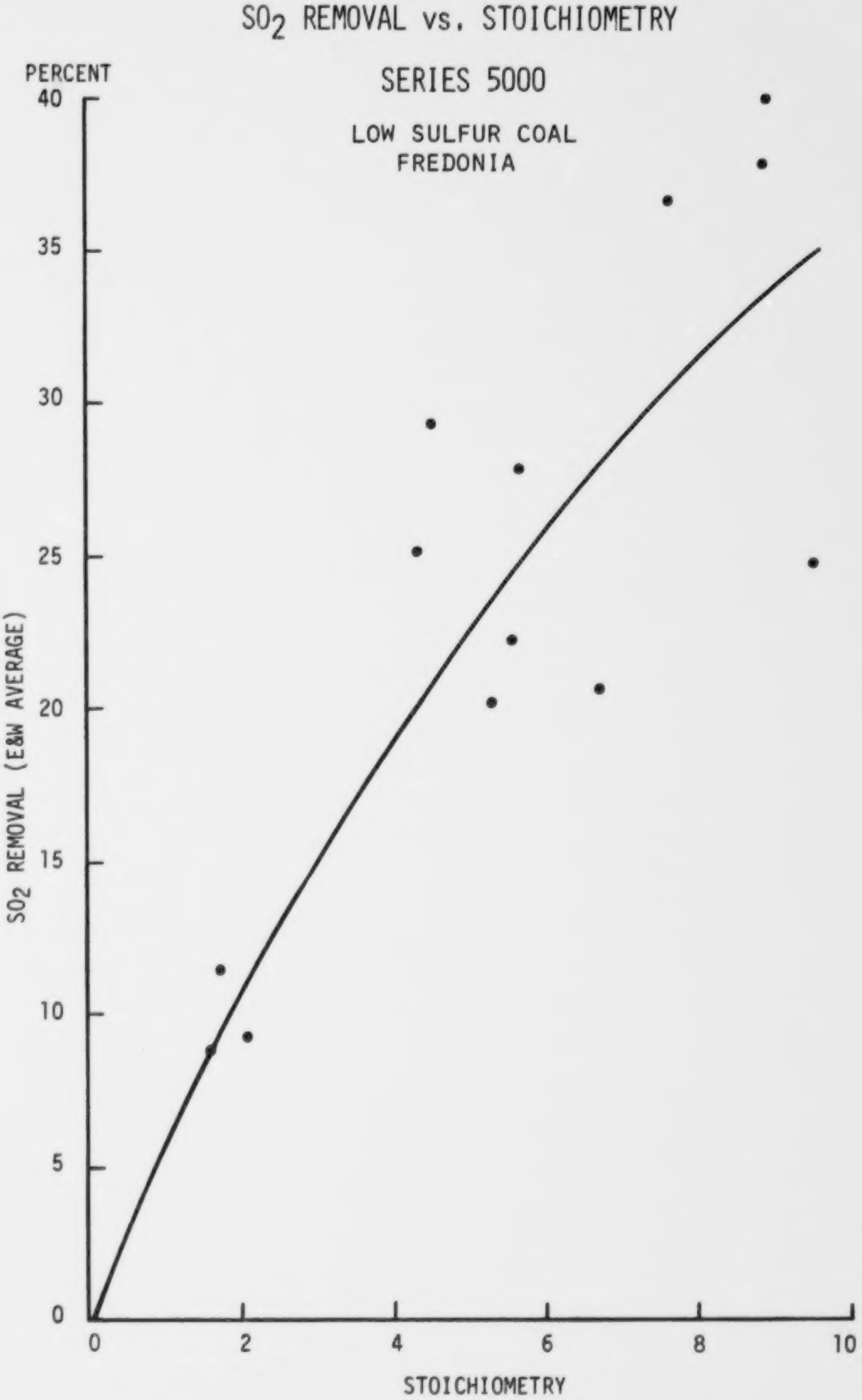

SO$_2$ REMOVAL vs. STOICHIOMETRY
SERIES 5000
LOW SULFUR COAL
FREDONIA
PERCENT
SO$_2$ REMOVAL (E&W AVERAGE)
0
5
10
15
20
25
30
35
40
0
2
4
6
8
10
STOICHIOMETRY

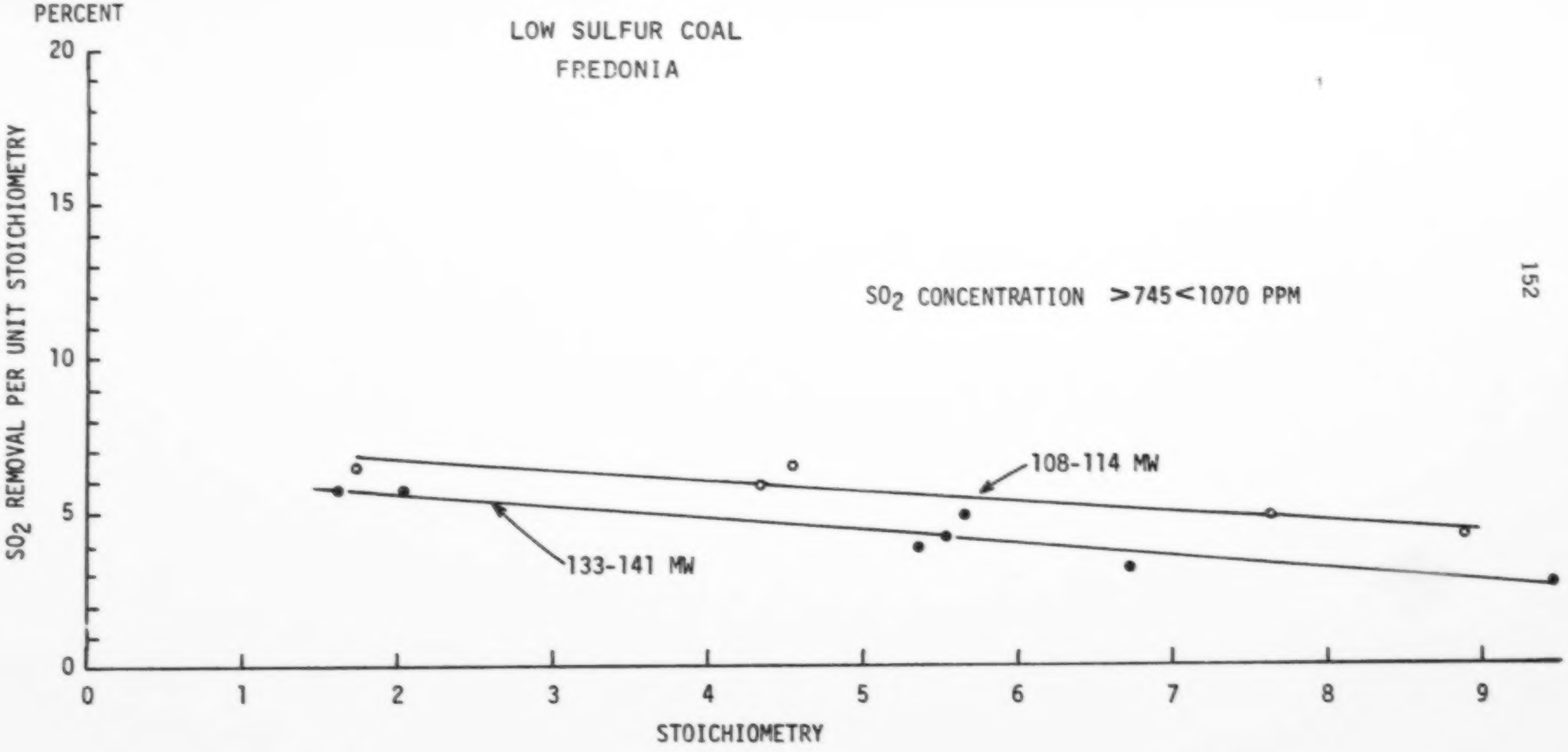
FIGURE 82

SO_2 REMOVAL vs. STOICHIOMETRY

SERIES 5000

LOW SULFUR COAL

FREDONIA



SO_2 REMOVAL EFFICIENCY vs. INITIAL SO_2 CONCENTRATION

SERIES 5000

LOW SULFUR COAL, FREDONIA

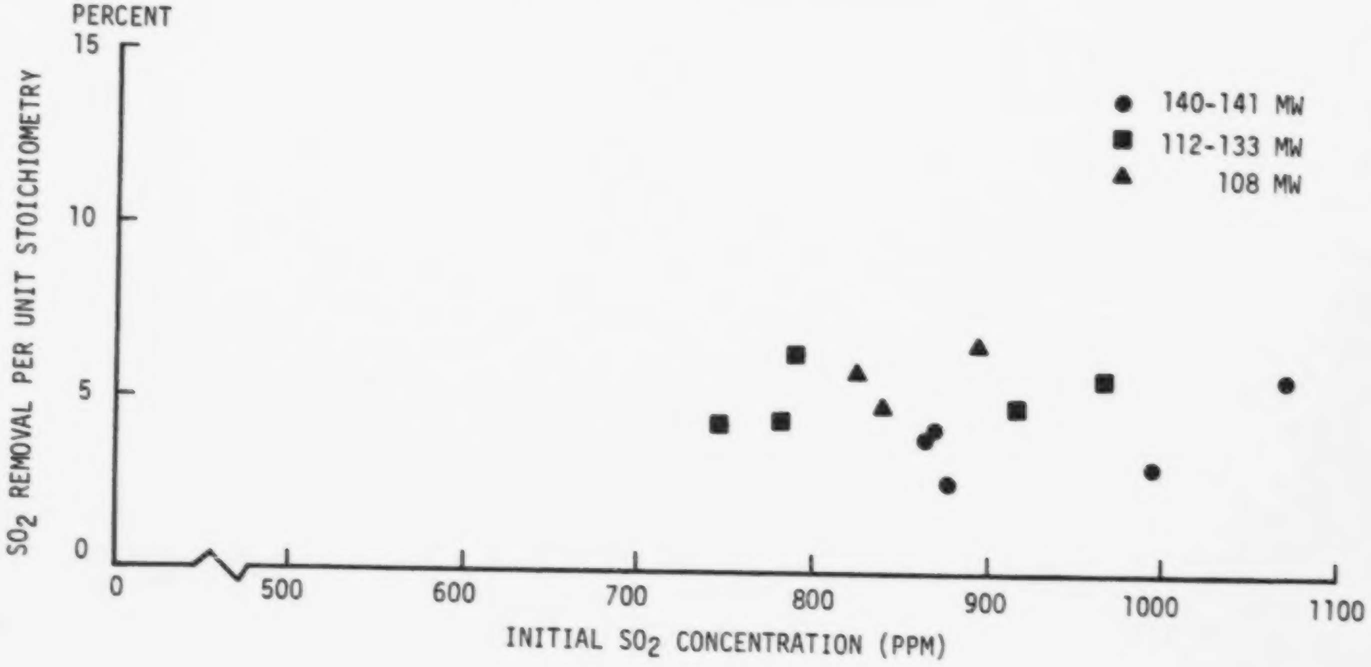


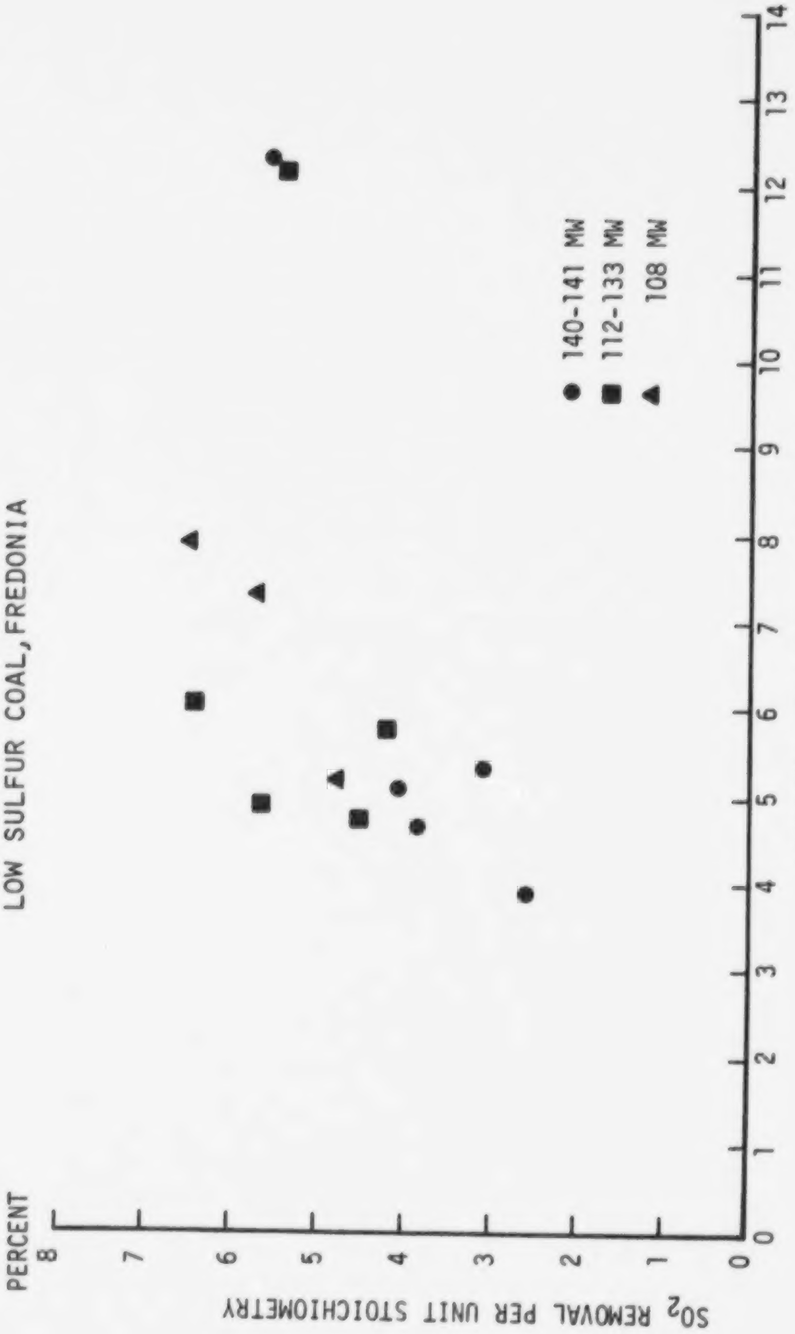
FIGURE 83

FIGURE 84

SO$_2$ REMOVAL EFFICIENCY vs. LIMESTONE UTILIZATION

SERIES 5000

LOW SULFUR COAL, FREDONIA



c. Particle Residence Time

Research studies by Babcock & Wilcox Co.[15], Battelle Memorial Institute[13], and results of initial tests at Shawnee indicated 2100 °F was about the most favorable temperature for dry limestone injection. Because the sulfation reaction practically ceases below 1700 °F and deadburning may begin above 2200 °F, it was important to know particle residence time in this range.

Calculated residence times were determined by Clay[22] on the basis of furnace dimensions, free flow areas in superheaters and reheaters, and gas mass flow rates. Mean gas flow paths were segmented into temperature zones. Actual temperature measurements were made by probes at elevation 348 (between B & C burner rows) and at Planes A-A, B-B, C-C.

Typical results obtained for the gas temperatures calculated at various locations along the flowpath are:

Table 16

TYPICAL GAS TEMPERATURES IN UNIT 10 AT FULL LOAD

Location	Gas Temperature °F
EL 347',6" lower rear injectors	2670
EL 359' 9" front injectors	2434
EL 364' 6" upper rear injectors	2342
EL 372' 0" beginning of boiler nose	2197
EL 376' 6" boiler nose (Plane AA)	2111
Front screen wall in superheater	2100
Center of secondary superheater(Plane BB)	1850
Exit of secondary superheater	1700
Entrance of reheater section	1550
Exit of reheater section	1350
Exit-first bank primary section	1150
Exit-second bank primary section	918
Rear screen wall in superheater	715

Measured temperatures and velocities at the Plane B-B for the last four series of optimization tests were as follows:

Table 17

PLANE B-B GAS TEMPERATURES AND VELOCITIES

Series	Load MW	Gas Temp. °F average E	W	Gas Velocity ft./sec. E & W avg.
2000 Marl	140 75	1601 1227	1528 1338	26.9 18.6
3000 Fredonia	75	1279	1174	19.9
4000 Argonite	140 75	1561 1440	1557 1132	29.7 23.5
5000 Fredonia	133-141 108-114	1498 1510	1555 1345	27.9 24.3

Residence time calculations made for both east and west furnaces in the temperature range 2200 °F to 1700 °F result in the following values:

Table 18

RESIDENCE TIMES IN REACTION ZONE

Series	Load	Residence Time Avg. E & W sec.	Stoich. (Avg.)	SO_2 Removal (Avg. E & W) %	No. of Tests
Aragonite	Full	0.89	1.8	13.1	6
Marl	Full	0.905	2.2	20.1	10
Fredonia	Full	0.95	2.1	19.5	26
Fredonia	Low (AB)	1.18	1.6	22.6	6
Aragonite	Low (CD)	1.275	2.4	18.9	6
Marl	Low (CD)	1.365	3.0	41.7	5
Fredonia	Low (CD)	1.625	2.6	30.6	8

Although results are only summarized above, the detailed results appeared to have several anomalies in that: (1) the residence times calculated for the west half of the furnace were consistently lower than those of the east half while removals, on the average, are higher for the west half; and (2) the ordering (or listing) induced by residence times does not agree with the ordering by removals, and in most cases, the discrepancies are not accounted for by stoichiometric differences.

Assuming zero removal in zero residence time, the data was grouped by load for each of the stones tests. Centroids of each group plus the origin (0, 0) yield the curves shown in figure 85. Some differentiation of SO_2 removal efficiency and particle residence time appears at 0.9 second. Trends are quite well confirmed by about 1.2 seconds. These curves show the apparent greater sensitivity of marl to the time-at-temperature condition, somewhat less for Fredonia and the least for aragonite. This confirms laboratory results for marl as reported elsewhere[16].

Average gas velocity ranges as determined by Plane B-B probes are shown in figure 86.

d. Overall Phase III Results

The comparative SO_2 removal capability of Fredonia, marl, and aragonite is shown in figure 87. These curves are plotted for full load (140 MW) and half load (75 MW) conditions while injecting fine particle size stone. The effect of boiler load is apparent in that low load provided more SO_2 removal. The percentage improvement in removal was largest for marl, less for Fredonia, and least for aragonite as load was dropped from 140 MW to 75 MW.

Removals increased for each stone type as stoichiometry increased.

The effect of initial SO_2 concentration is shown in figure 88 for both full and half load conditions. Each curve represents average SO_2 removal efficiency over the range of concentrations encountered in the series. At 140 MW load, higher removal efficiency was obtained with Fredonia at higher SO_2 concentrations. There was insufficient range in SO_2 concentrations, at given load conditions, for either the marl or aragonite to assess SO_2 concentration effects but it probably would not have affected aragonite significantly.

The effects on SO_2 removal efficiency caused by load, stoichiometry, and limestone type changes are clearly shown in the above. Other controlled variables such as particle size, injection velocity and angle, and excess air were statistically insignificant for the ranges tested. Results of the statistical treatment were as follows:

1. For all tests in the optimization series, stoichiometry was the major controlling variable in SO_2 removal.
2. Boiler load, as it affects residence time, is a prime factor in SO_2 removal efficiency.
3. Particle size is of secondary importance as an independent variable. However, the particle size—stoichiometry interaction was found to be a prime factor. Smaller particle size gave improved SO_2 removal in the Series 1000 tests. (Refer to figure 89.)
4. When injecting marl limestone at 50% load, the SO_2 removal efficiency increased to about 21%, at 1X stoichiometric.
5. When burning low sulfur coal (1000 ppm SO_2) at full load of 140 MW, the % SO_2 removal efficiency was about 4%. At lower load (108 MW) and burning low sulfur coal (1000 ppm SO_2) the SO_2 removal efficiency was approximately 5%.
6. The average standard error (S_x) for all tests was about 4%. Table 19 is a summary of the statistical analysis performed on the optimization tests.

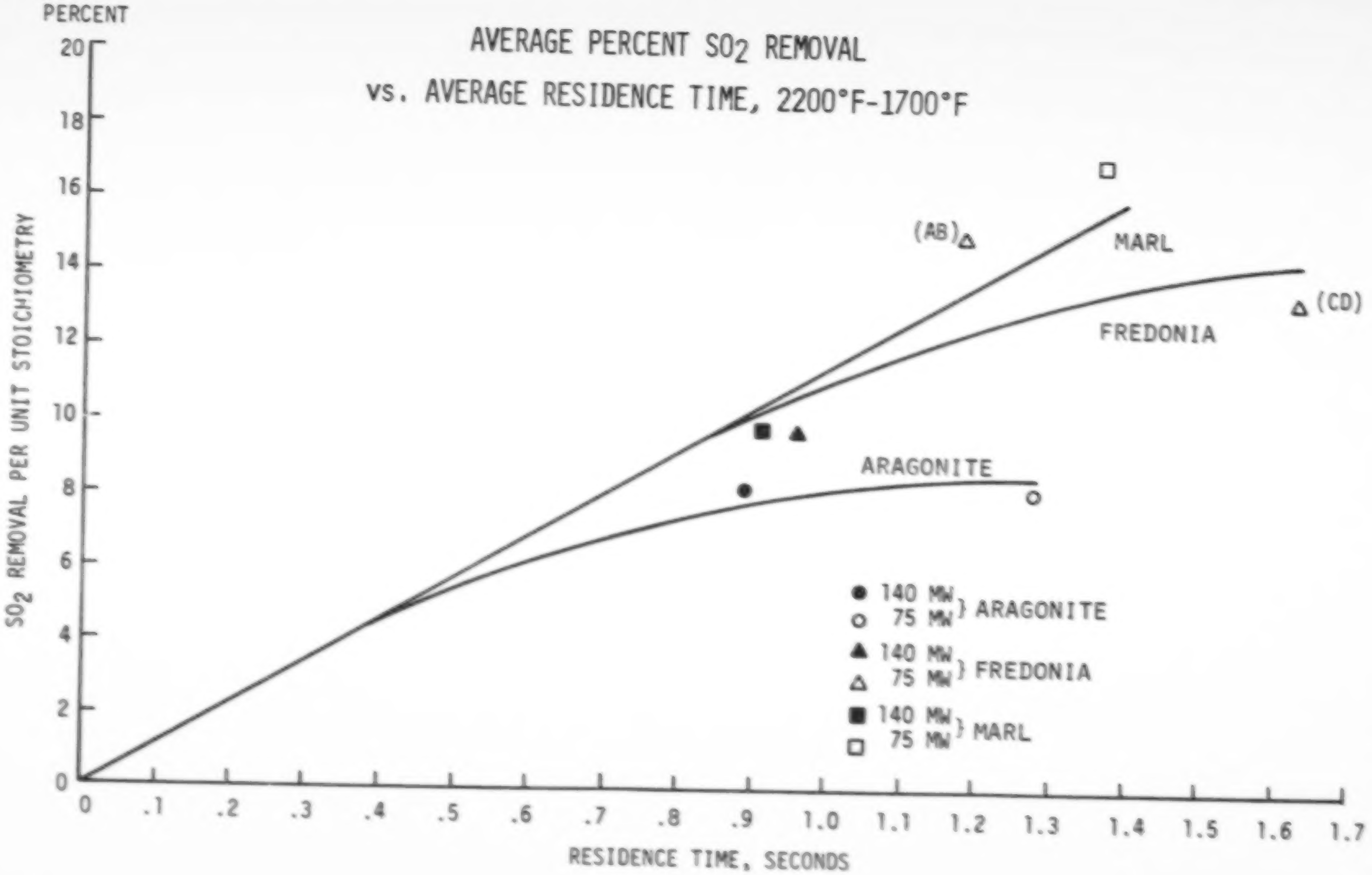
Table 19

OPTIMIZATION TESTS
SUMMARY SHEET
Statistical Analysis

			Analysis of Variance							
		T-statistics for	Source	Degree of Freedom	Sum of Squares	Mean Square	F-ratio	R	R^2	St'd Error
Series 1000 Fredonia	East and West separate observations *$\% SO_2 = 3.55 + 10.3X_1 - 0.563 X_1 X_2$ where X_1 = stoichiometry X_2 = particle size	$X_1 = 7.5927$ $X_2 = -2.5993$	Regression	2	2585	1293	50.7	.827	.684	5
			Residual	47	1198	25.49				
			Total	49	3783					
Series 2000 Marl	East: $\% SO_2 = 9.36 + 6.98X_1 - 6.16X_2$ where X_1 = stoichiometry X_2 = load = ±1	$X_1 = 10.7681$ $X_2 = -5.3664$	Regression	2	3072	1535.8	93.74	.97	.94	
			Residual	12	196					
			Total	14	3268					
	West: $\% SO_2 = 11.51 + 8.64X_1 - 7.78X_2$		Regression	2	4587	2293.5	51.8			
			Residual	12	530	44.2		.95	.90	4
			Total	14	5117					
Series 3000 Fredonia	East: $\% SO_2 = 9.61 + 6.92X_1$ where X_1 = stoichiometry	$X_1 = 3.9278$	Regression	1	851	851	15.4	.84	.71	8
			Residual	11	606	55.1				
			Total	12	1457					
	West: $\% SO_2 = 11.32 + 9.03 X_1$	$X_1 = 5.1309$	Regression	1	1450	1450	26.3	.76	.58	
			Residual	11	606	55.1				
			Total	12	2056					
Series 4000 Aragonite	E - W Response $\% SO_2 = 7.05 + 8.36X_1 - 0.678X_1X_2$ where X_1 = stoichiometry X_2 = particle size	$X_1 = 6.4830$ $X_1X_2 = -3.3844$	Regression	2	1125	562.5	70	.95	.90	2.8
			Residual	14	112	8				
			Total	16	1437					
Series 5000 Low S Coal	Average E + W $\% SO_2 = 41.12 + 3.217X_1 - 0.2747X_2$ where X_1 = stoichiometry X_2 = load	$X_1 = 6.4830$ $X_2 = -2.9148$	Regression	2	1061	530.5	24	.91	.83	4.5
			Residual	10	220	22				
			Total	12	1281					

Note: *$\% SO_2$ refers to removal

FIGURE 85



AVERAGE PERCENT SO_2 REMOVAL

vs. AVERAGE RESIDENCE TIME, 2200°F-1700°F

FIGURE 86

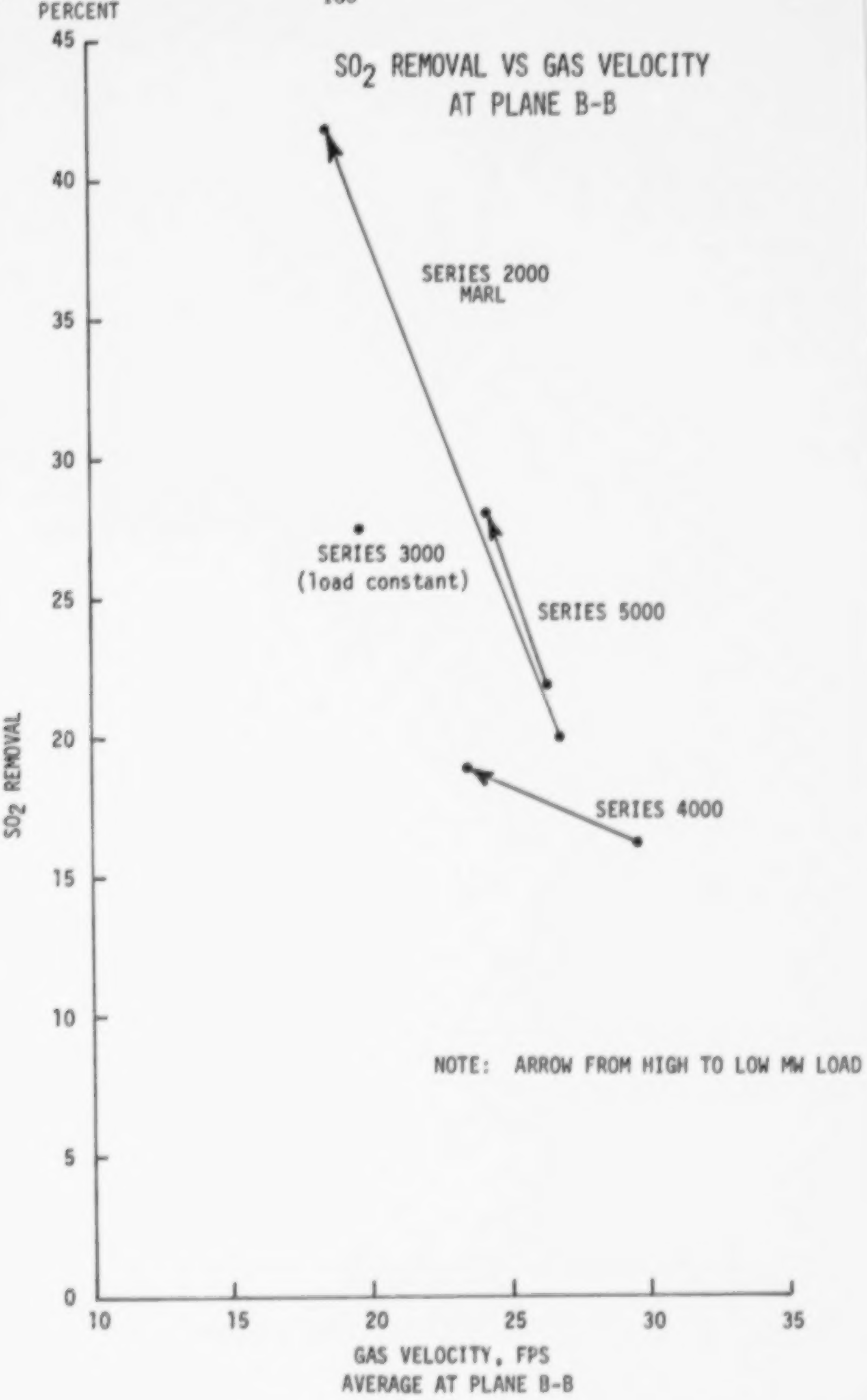

PERCENT
SO$_2$ REMOVAL VS GAS VELOCITY
AT PLANE B-B
45
40
35
30
25
20
15
10
5
0
SO$_2$ REMOVAL
SERIES 2000
MARL
SERIES 3000
(load constant)
SERIES 5000
SERIES 4000
NOTE: ARROW FROM HIGH TO LOW MW LOAD
10
15
20
25
30
35
GAS VELOCITY, FPS
AVERAGE AT PLANE B-B

FIGURE 87

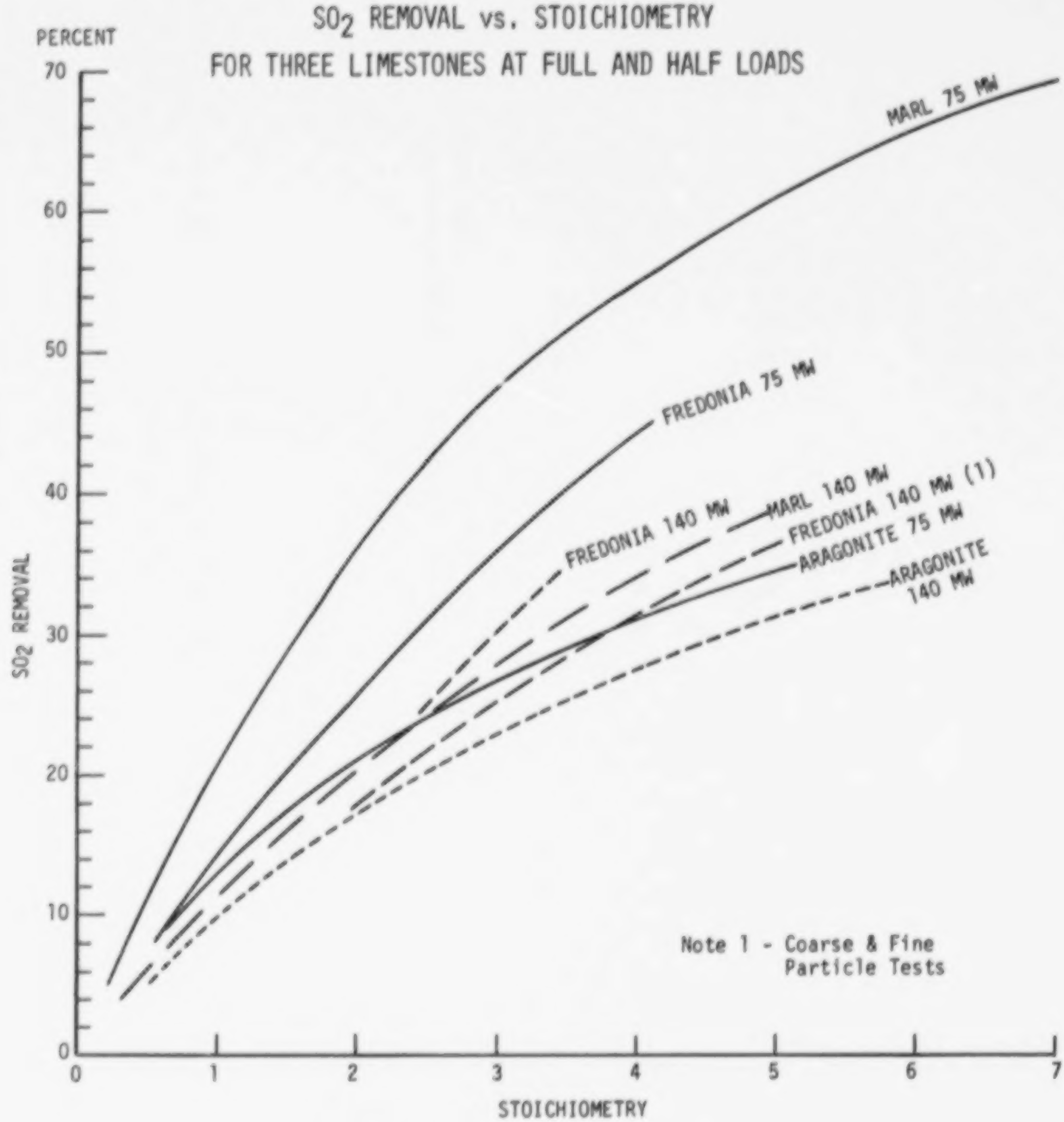
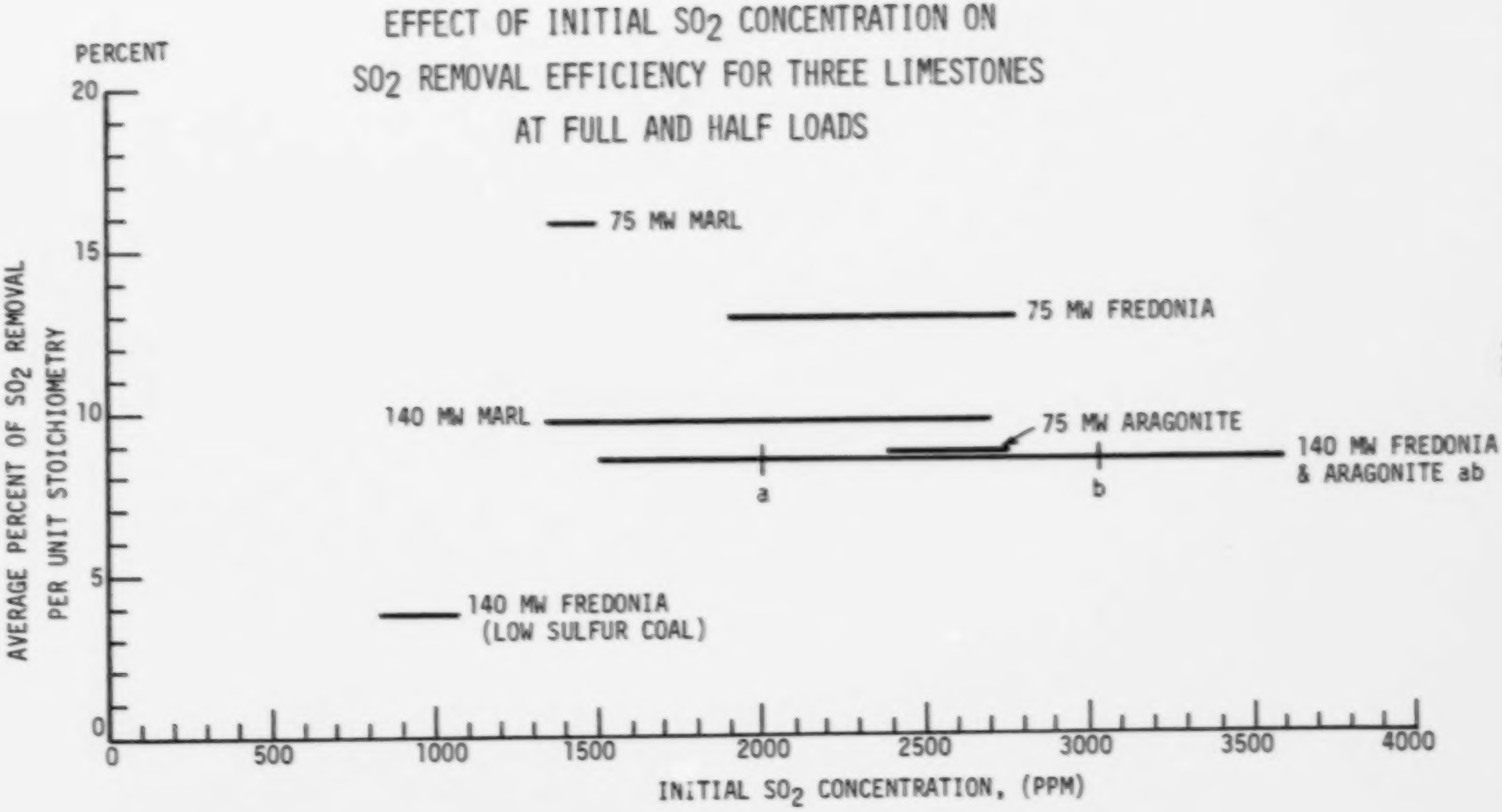
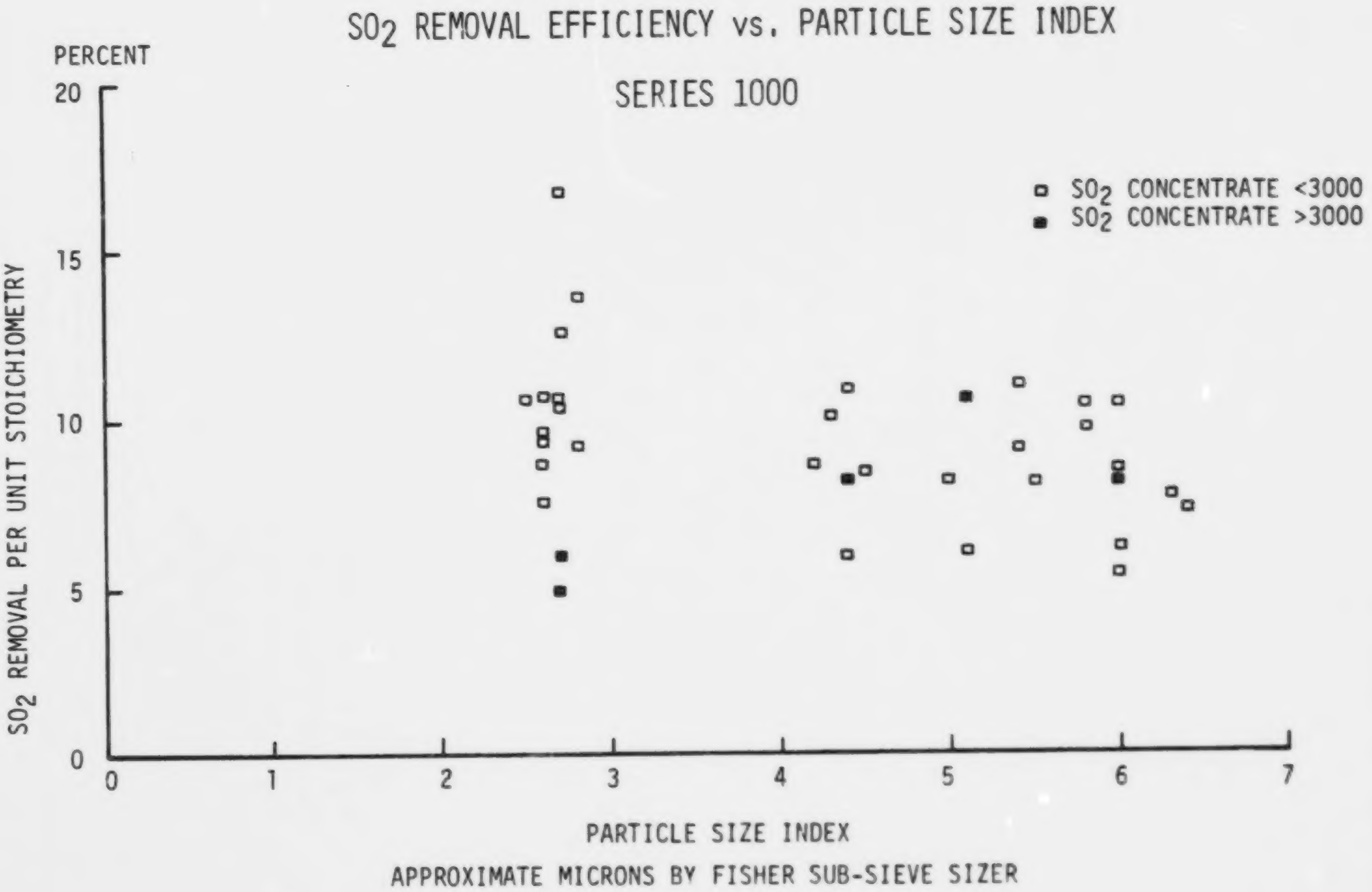

SO$_2$ REMOVAL vs. STOICHIOMETRY
FOR THREE LIMESTONES AT FULL AND HALF LOADS
PERCENT
70
60
50
40
30
20
10
0
SO$_2$ REMOVAL
0
1
2
3
4
5
6
7
STOICHIOMETRY
MARL 75 MW
FREDONIA 75 MW
FREDONIA 140 MW
MARL 140 MW
FREDONIA 140 MW (1)
ARAGONITE 75 MW
ARAGONITE 140 MW
Note 1 - Coarse & Fine Particle Tests

FIGURE 88



EFFECT OF INITIAL SO_2 CONCENTRATION ON SO_2 REMOVAL EFFICIENCY FOR THREE LIMESTONES AT FULL AND HALF LOADS

FIGURE 89



SO_2 REMOVAL EFFICIENCY vs. PARTICLE SIZE INDEX

SERIES 1000

A total of 75% of the variability of SO_2 removal can be attributed to stoichiometry and an additional 15% is attributed to the interaction of stoichiometry and particle size. About 1% in SO_2 removal efficiency was gained in moving the injection location from upper rear to the plane A-A. Most of the gain made by reducing deadburning by injection at plane A-A seems to have been offset by loss of residence time in the most favorable temperature region.

4. CONCLUSIONS

a. Prime Factors - Stoichiometry and Residence Time

The optimization tests showed that stoichiometry independently, and through interaction with particle size, was the most significant factor affecting SO_2 removal. More limestone present in the gas removes more SO_2. The smallest size particle available produced the best removals.

Operating difficulties such as plugging obviously limit limestone inputs. Particle size also reaches an optimum minimum by reason of grinding economics and reduced particle pore surface transformations that occur when small particles are subjected to furnace gas conditions.

b. Residence Time

Increasing the residence time (by reducing load) improved SO_2 removal efficiency (% SO_2 removal/unit stoichiometry) for marl, Fredonia, and aragonite limestones. Within data limits, marl showed continued improvement whereas Fredonia and aragonite leveled earlier. These differences are attributed to physico-chemical properties of the stones since all were subjected to similar trials.

The fact that only a relatively short time period is available in a boiler at temperatures favorable for the reaction it does not explain why the process is inefficient. It appears that the process is self-limiting. The reaction is limited by the rate of chemical reaction which, in turn, is limited by the rapid loss of surface area (due to grain growth and blockage by reaction products) immediately following calcination. (See appendices I and J, Volume 3.)

This self limiting aspect of the reaction necessarily defeats any attempt to significantly improve performance by manipulation of process variables.

Optimum time-at-temperature appears achievable by injection above the maximum combustion zone. Aragonite injected at the upper rear during earlier trials showed better removal than when injected at the plane A-A. Analyses indicated that aragonite injected at plane A-A was not completely calcined. Therefore, it is expected that performance with this stone benefits from the higher temperature and longer residence time associated with upper rear injection.

c. Limestone Type

The value of using one type over another was evaluated to a limited extent in this optimization phase. Even stones selected as possibly being the best have displayed comparatively poor SO_2 removals at low and practical stoichiometries. High inherent moisture of marl results in difficult handling problems with resulting high cost. All three stones showed improved SO_2 removal as stoichiometry increased but at full load condition on the boiler the three stones tested only removed 17% to 20% of the SO_2 at 2X stoichiometry.

d. Injection Angle and Velocity

Dust distribution is determined by furnace gas turbulence and aside from injection elevation the factors of angle and velocity, per se, have slight influence on SO_2 removal. The limestone plus its transport air represent a few percent of total mass flow into the furnace so influence turbulence accordingly little. Velocities achieved here appear adequate to accomplish both the transport function and assure uniform dust distribution. The number of nozzles employed was reasonable. The use of steam to boost injection velocity could not be identified as helping SO_2 removal.

e. SO_2 Concentration

Recorded initial SO_2 values during the test series ranged from a low of 860 ppm to a high of 3460 ppm. Lower SO_2 removal efficiency was achieved at lower initial SO_2 concentrations thus confirming full-scale what had been predicted from laboratory tests i.e., the initial reaction is first order with respect to concentration.

The average initial SO_2 concentrations plotted against SO_2 removal efficiency for tests in each of these series are shown in figures 90, 91, 92, 93, and 83 previously mentioned.

FIGURE 90

SO$_2$ REMOVAL EFFICIENCY vs. INITIAL SO$_2$ CONCENTRATION

SERIES 1000

FREDONIA FULL LOAD

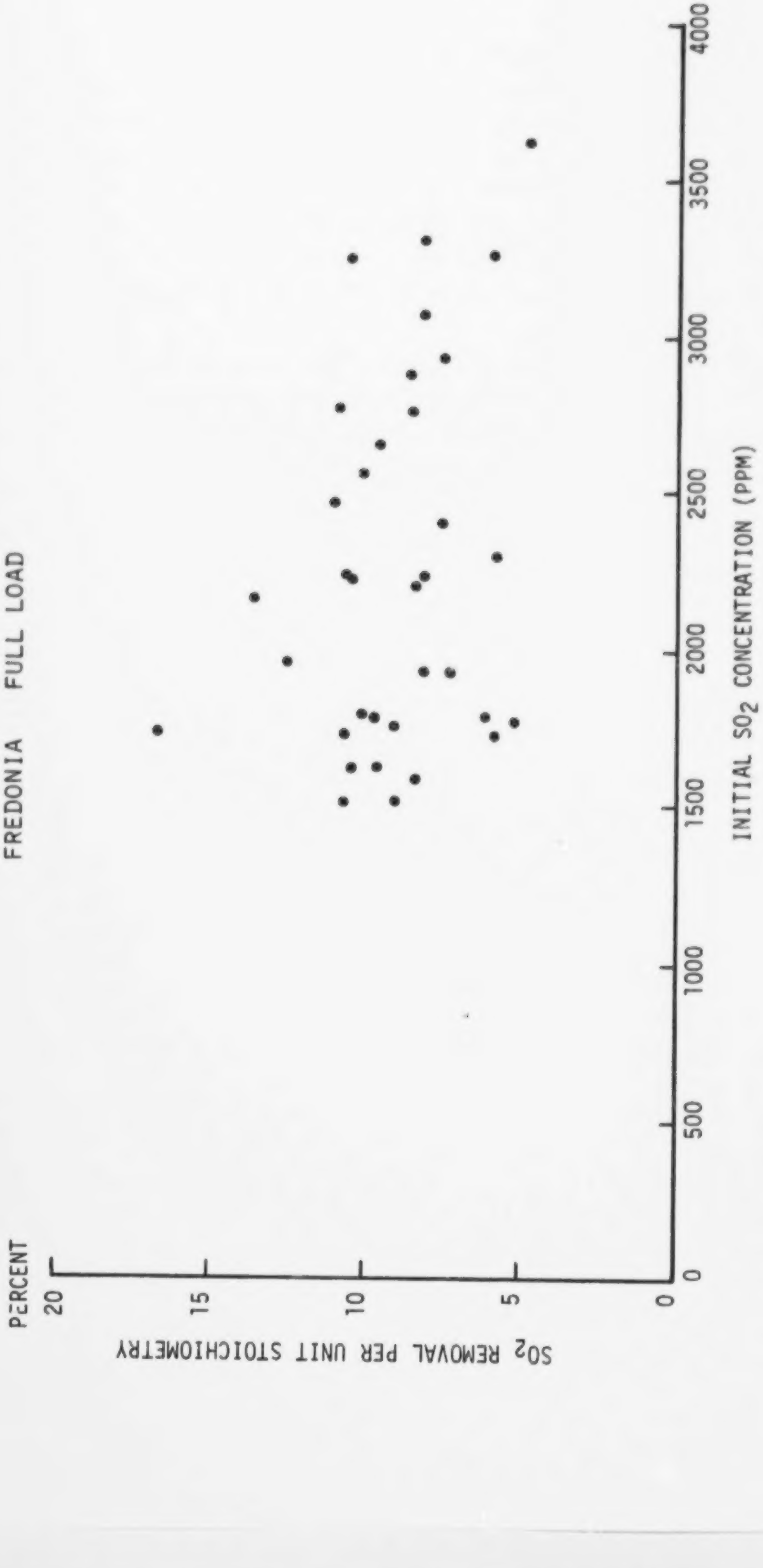


FIGURE 91

SO_2 REMOVAL EFFICIENCY vs. INITIAL SO_2 CONCENTRATION

SERIES 2000

MARL

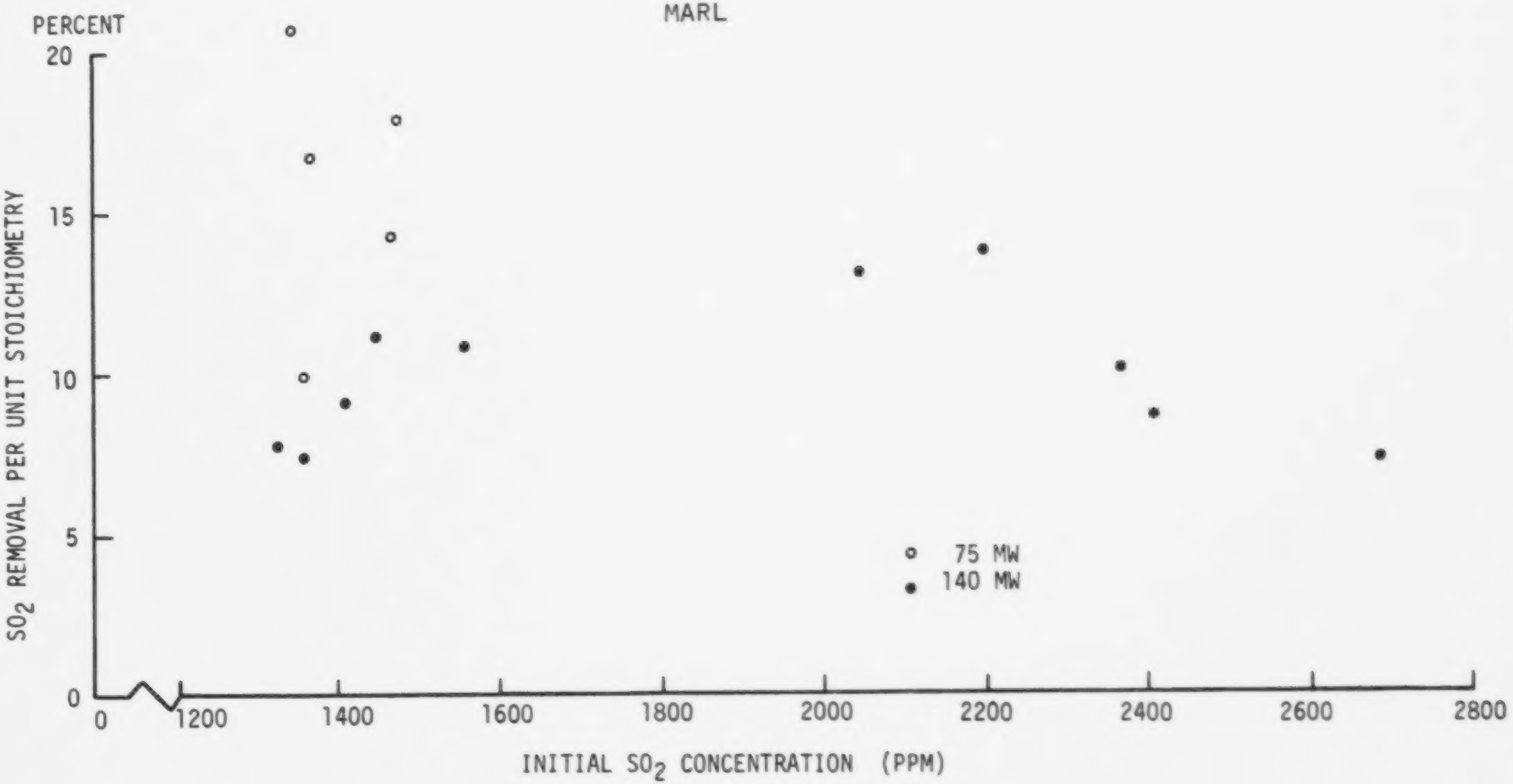
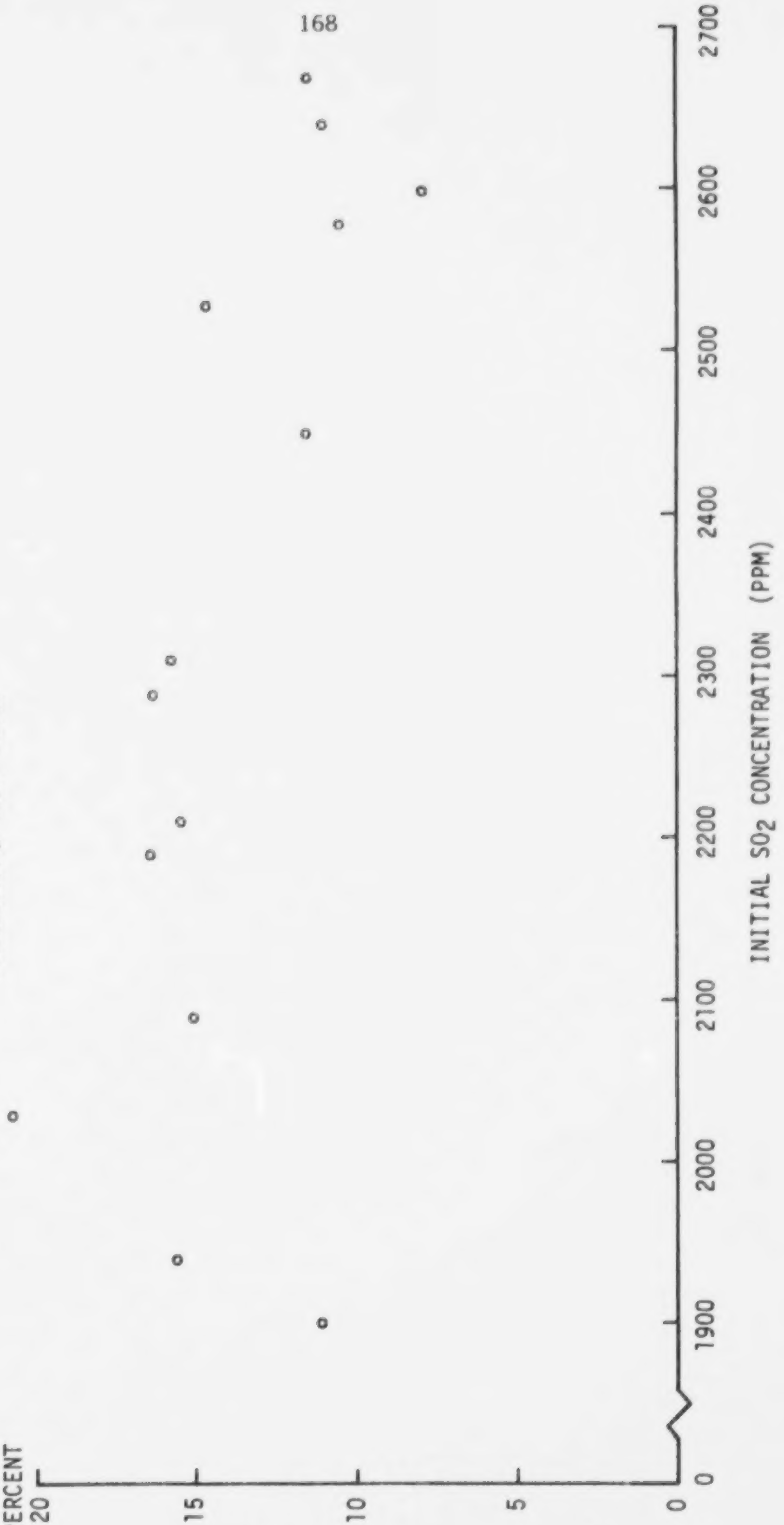


FIGURE 92



SO$_2$ REMOVAL EFFICIENCY vs. INITIAL SO$_2$ CONCENTRATION

SERIES 3000

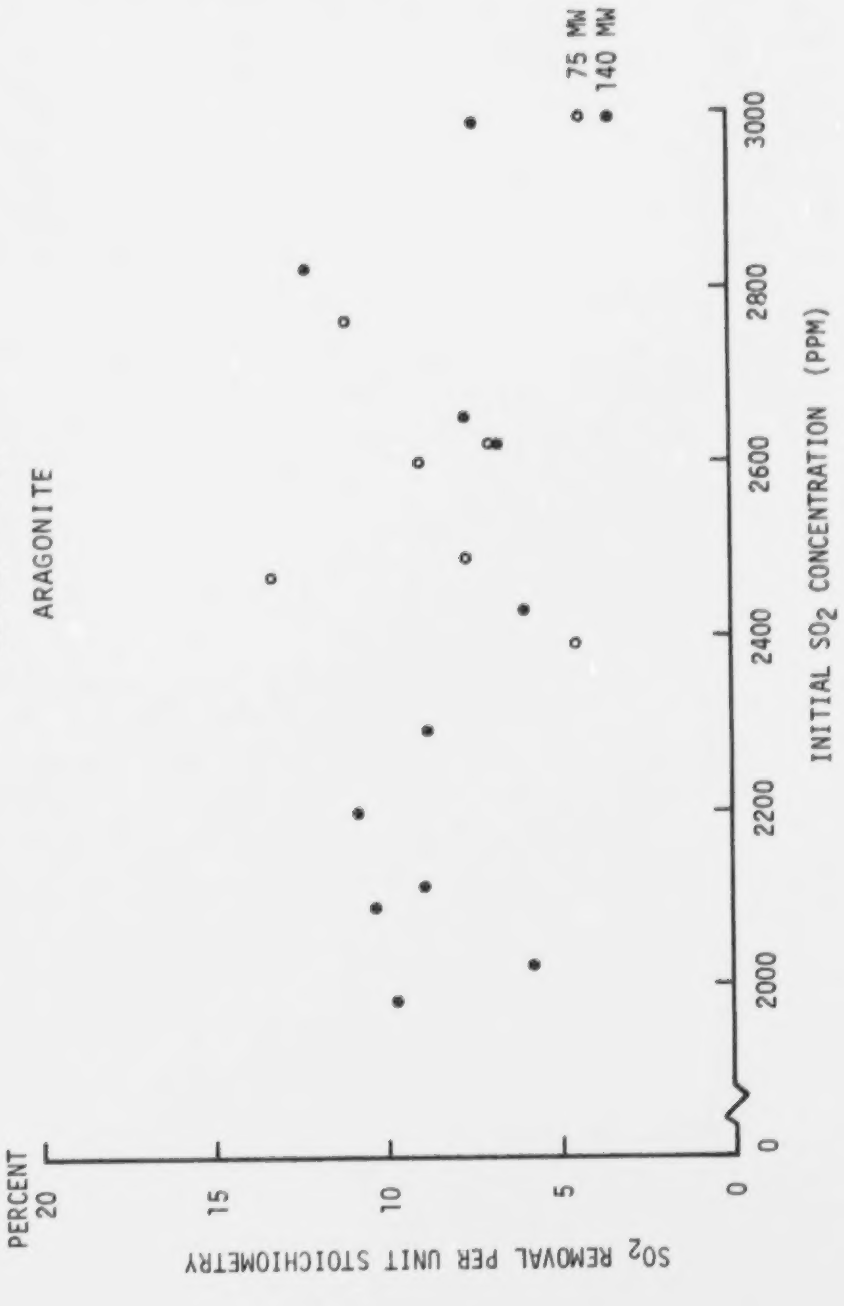
FREDONIA, LOW LOAD

FIGURE 93

SO_2 REMOVAL EFFICIENCY vs. INITIAL SO_2 CONCENTRATION

SERIES 4000

ARAGONITE



F. PHASE IV. LONG-TERM OPERATION

1. OBJECTIVES

The purpose of Phase IV was to operate at the optimized injection conditions, determined during Phase III, for a period sufficient to determine the process effects on:

a. Boiler operation and efficiency

b. Precipitator operation and efficiency of the solids sluice system when handling the fly ash-limestone mixture.

c. Waste water quality

d. Equipment reliability and performance in terms of maintenance requirements as influenced by erosion/corrosion.

e. Cost for operating the drying, grinding, and limestone handling equipment

f. Long-term removal of SO_2

Six months of continuous limestone injection was originally considered necessary but later program evaluation indicated, with exception of erosion/corrosion effects and precipitator performance, the objective could be met in six weeks. This schedule revision was essentially based on data accumulated during earlier program phases. A review of prior erosion and corrosion history showed that at least 12 months operation would be required for proper evaluation of these effects. Informal consultation with Research-Cottrell and others knowledgeable in precipitator operation indicated that after initial effects on precipitator performance no further degradation with time was expected while limestone injection for SO_2 removal was underway.

2. APPROACH

The results of Phase III optimization tests would be applied to phase IV, where possible, so that long term optimized conditions would prevail. However, several events occurred which prevented full use of optimized conditions and carrying out the original goals of Phase IV. These events caused variations as follows:

- Use of coarse particle size rather than the optimized fine particle size because of reduced mill capacity for fine grinding.
- Burn coal from a single source instead of off-the-pile or unregulated source coal because of need to stabilize ash properties.
- Reduce stoichiometry of limestone feed from 2X to 1X as a result of reheater and hydroveyor plugging experienced during Trial 1.
- Inability to obtain long term effects type of data because only two brief injection periods were realized.

a. Test Design

Plans called for 6 weeks of continuous limestone injection under the optimum conditions obtained from Phase III. A reduced sampling and measurements program was carried out since there was greater interest in monitoring and inspection activities. Results of Phase III optimization tests indicated that fine particle, Fredonia limestone injected at -25 degree angle through six nozzles at the plane A-A would be optimum with stoichiometries up to about two.

Changes to the original approach came about after the start of Trial 1 in August 1971 when sluicing problems developed. At the time, Shawnee's sluice system had not been upgraded to cope with the increased fly ash burden caused by installation of precipitators. At the planned 2X stoichiometric feed rate the Unit 10 ash burden doubles and adds about 9% to the total system; at 1X stoichiometric it adds 5%. Operation of sluicing facilities trailed requirements even though the original 2X was reduced to 1X stoichiometric shortly after starting long-term injection. This condition persisted at the reduced injection rate even though hydroveyors were cleaned after each sluice cycle.

Experience gained during Trial 1 resulted in some changes in the approach to Trial 2, conducted in January 1972. Each change is discussed in the following paragraphs.

Mill Capacity

The existing mill does not have capability of grinding enough fine particle size stone to meet requirements of full-load, 2X stoichiometric injection rates. Capability drops from 20 TPH on coarse size down to about 6 TPH on fine. For this reason coarse size was accepted for use during the long-term injection and ranged from 5 to 6 microns (Fisher size). It is obtained at gyrotor classifier setting of 20% speed.

Coal Selection

Original plans called for burning the same kind of coal in Unit 10 as in the other Shawnee units. This would have added an important degree of freedom for the dry limestone injection process applied to an existing unit. However, the problem of pluggage caused this approach to be dropped since it was suggested that restricting the coal type would minimize changes in ash fusion temperature and ash constituents both of which influence plugging. It was understood that the coal selected (Old Ben Mines 24 and 26) was not the best with respect to ash characteristics but unit train quantities would assure more uniform ash properties.

During Trial 1 there was no restriction on coal type but for the above mentioned reasons testing was confined to single source coal during Trial 2.

Sampling

A reduced sampling program was carried out during this period but did include:

One daily bunker sample of coal for determination of total sulfur content.

One sample per shift of limestone from the feed tank for assay of CaO and particle size index.

One composite fly ash sample obtained during each shift from the six sample points located in the boiler outlet plane C-C. Chemical analyses were run to determine %S, %CaO, %CO_2 plus % hydration and utilization.

Samples were taken of fly ash-limestone deposits that formed in sluice system hydroveyors.

Measurements

Perhaps the principal item monitored during Phase IV was the pressure drop across the reheater tube pendants. It was recorded hourly along with other boiler data and was backed up by a series of manometers installed for close watch on pressure drop. Injection would be stopped when the drop reached 2" w.c.* at 140 MW load.

Oxygen measurements were made at the boiler outlet plane C-C.

Ultraviolet analyzers were operated continuously at plane C-C for measurement of the SO_2 concentration. This was required for determination of limestone feed rate which was adjusted hourly to match coal sulfur variations and/or boiler load changes, explained below.

Soot blowing and sluicing

Increased soot blowing frequency was expected for Unit 10 during Phase IV. Comparative data on sootblower frequency was obtained on Units 2, 4, 6, 8, 9, and 10 during the test. More frequent or longer sluicing periods would also be required. Units 9 and 10 share a common sluice header and all ash is sent to a common sluice pond.

Stack gas monitor

It was planned that an optical monitor currently installed in the breeching between an induced draft fan and the stack would be operational to possibly verify the assumption that precipitator performance would not degrade with time. However, it was inoperative during the Phase IV tests. Prior to the start of testing the precipitator was checked for proper adjustment and daily log sheets kept of important values.

b. Test Procedure

Limestone feedrate

The design called for 2X stoichiometric feedrate and the boiler operator was given the feeder speed percentage setting each hour. Test personnel derived this value as a function of load and SO_2 level. During Trial 1 the feeder was stopped briefly once each shift to obtain the noninjection SO_2 level from which feedrate could be calculated. This procedure was altered for Trial 2 when the feeder was not stopped and the limestone feedrate was based on an assumed 10% SO_2 removal per unit stoichiometry. The feedrate in Trial 2 was limited to 1X stoichiometric and up to 11,000 lb./hr. at 140 MW and above. If an hourly adjustment required less than a ± 10% change in feedrate then it was not changed for the next hour. The continuous feeding followed a Babcock & Wilcox recommendation given to reduce rate of tube slag formation.

Observations

Test personnel maintained a log of activities requiring special attention during the injection period. They noted necessary repairs and particularly the periods of hopper sluicing and hydroveyor cleanout. It became necessary to hand clean hydroveyors after completing each precipitator and mechanical fly ash hopper sluice cycle.

The effects of limestone injection on waste water disposal were studied by TVA's Water Quality Branch. The data collected during the long-term injection is somewhat limited. The results on water quality analysis are discussed in appendix G.

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*w.c. means water column.

Data required for assessing operating costs involved limestone inventories and reading watt hour meters connected to various groups of process equipment.

Operating comparisons

Although not identified as an objective, per se, another important activity would be comparisons between Shawnee operating experience and that of other investigators. This would revolve primarily around coal ash slagging properties, where deposits occurred and means of removing them. The Power Metrology Research Organization "Energopomiar" in Poland[23], under an EPA Special Foreign Currency Program, performed "Research into the effect of introducing dolomite into boilers on the disposition of coals to form deposits on heating surfaces." The Polish results are not reviewed in this report.

3. TEST RESULTS

There were two periods or trials at long-term operation. Trial 1 took place between August 9 and 19, 1971, while Trial 2 occupied the period January 2-9, 1972. Two trouble spots developed during these trials; (1) development of excessive gas side pressure drop in the reheater and (2) plugging of hydroveyors located in the mechanical collector and precipitator sluice lines. Because these were the major factors resulting in termination of each trial they are discussed in considerable detail below.

These brief injection periods obviously revealed the major problems but also diminished possibilities of getting data sought as Phase IV goals. Potentiality of reheater plugging was reaffirmed after the outages of mid-May and October 1971 to clean the reheater because of pressure drop increases. These deposits had been formed under conditions of varying load, intermittent and variable limestone feed rates. The hydroveyor problem had not revealed itself during earlier phases because the intermittent injection periods did not overburden the sluice system though somewhat increasing sluice periods. Unit 10 reheater is shown in figure 94.

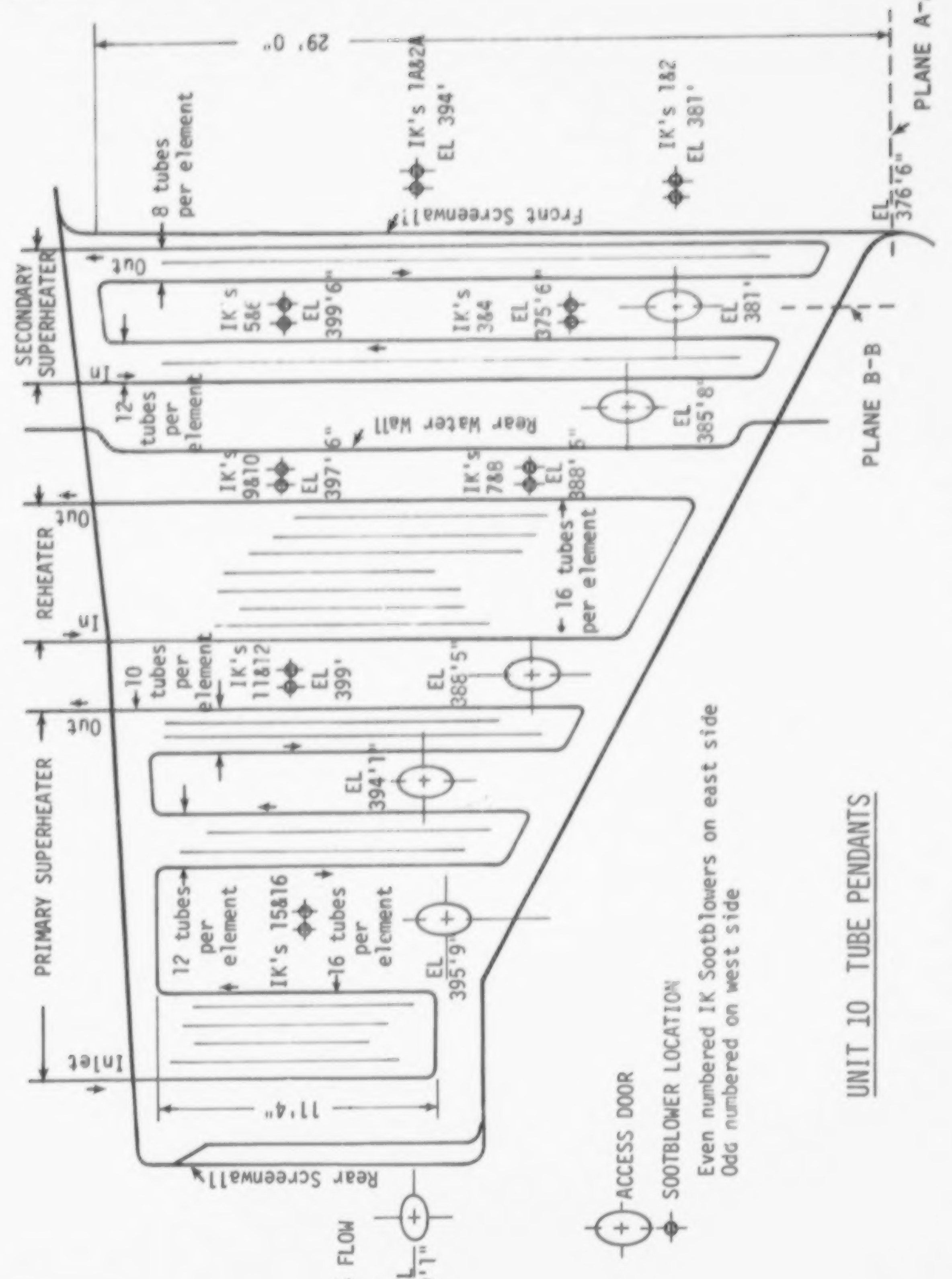
TRIAL 1

The data obtained during Trial 1 is summarized in table 20. The test began with 2X stoichiometric feed rate but was stopped after only 52 hours in order to completely empty Unit 10 fly ash hoppers and bottom ash. This cleanup was accomplished and limestone injection resumed at 1X stoichiometric for another 141 hours before reheater plugging developed which required a unit outage.

The initial 2X feed rate about doubles the solids loading. Deposits within the hydroveyors reduced their capacity and further burdened sluicing operations. The need for alternate sluicing of Units 9 and 10 caused cleanup operations to fall behind because even without limestone injection the sluice system was not designed to handle precipitator ash. The reduced feed rate of 1X stoichiometric alone would not have materially affected the sluice system.

As shown in figure 95, the reheater differential indicated no increase until the second day after resuming feed when the differential climbed rapidly. When the average differential reached 2" w.c. with no indication of stopping or relief from increased sootblowing, Trial 1 was terminated. Note that Unit 9, which consumed the same kind of coal as Unit 10 during Trial 1, did not experience any abnormal reheater plugging. Samples of tube deposits could not be obtained until the October outage. A total of 1,150 tons of limestone was injected during Trial 1.

FIGURE 94


29' 0"
PLANE A-A
PLANE B-B
IK's 1A&2A
EL 394'
IK's 1&2
EL 381'
8 tubes per element
Front Screenwall
EL 376'6"
SECONDARY SUPERHEATER
Out
In
IK's 5&6
EL 399'6"
IK's 3&4
EL 375'6"
EL 381'
12 tubes per element
Rear Water Wall
EL 385'8"
IK's 9&10
EL 397'6"
IK's 7&8
EL 388'5"
REHEATER
Out
In
16 tubes per element
10 tubes per element
IK's 11&12
EL 399'
EL 388'5"
PRIMARY SUPERHEATER
Out
EL 394'1"
12 tubes per element
IK's 15&16
16 tubes per element
EL 395'9"
Inlet
11'4"
Rear Screenwall
GAS FLOW
EL 399'1"
ACCESS DOOR
SOOTBLOWER LOCATION
Even numbered IK Sootblowers on east side
Odd numbered on west side

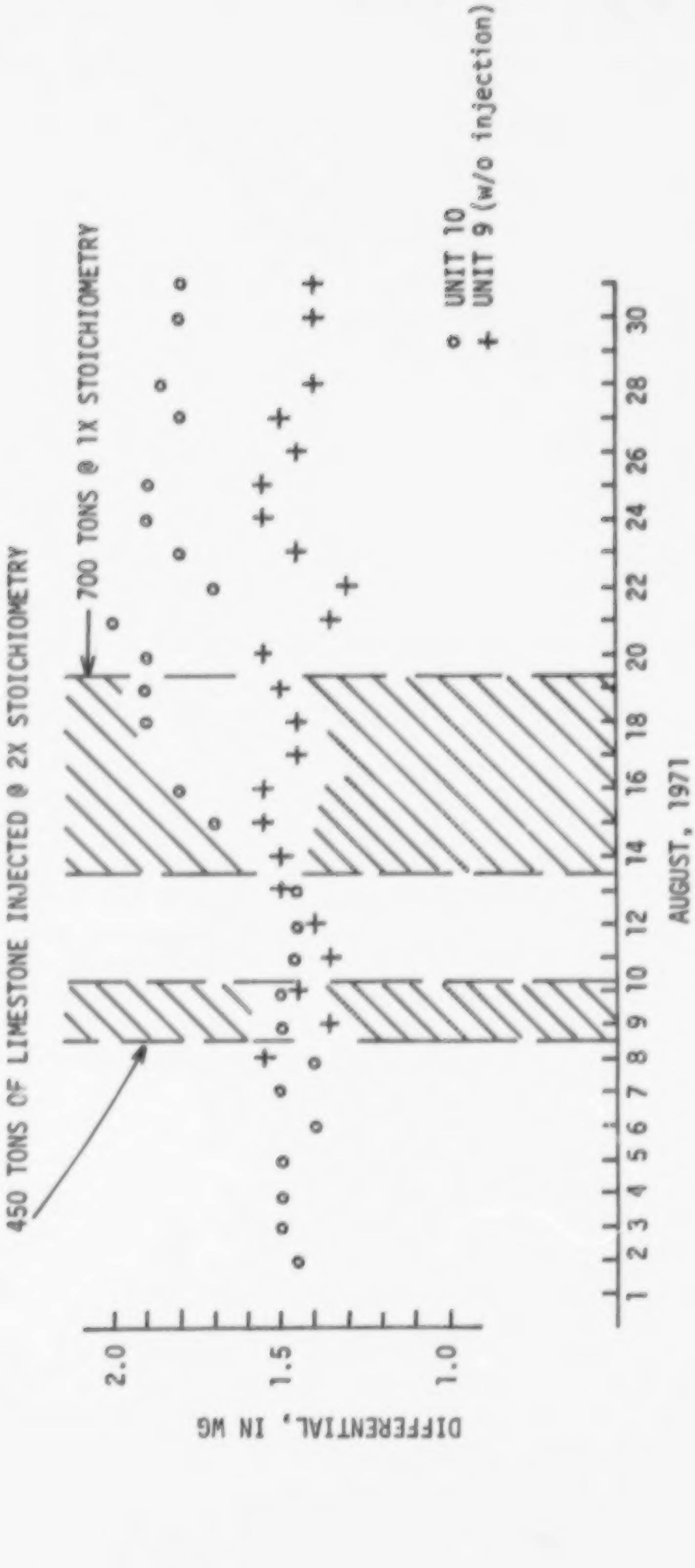
UNIT 10 TUBE PENDANTS

FIGURE 95

REHEATER DIFFERENTIAL

TRIAL 1 LONG TERM INJECTION

DIFFERENTIALS READ WITHIN ONE HOUR
AFTER BLOWING IK NUMBERS 7,8,9, & 10 AT LOADS
135-140 MW ON UNIT 10, 139-149 MW ON UNIT 9



ITEM NO.	DESCRIPTION				
1.	For Data Taken (Date)	AUG. 9, 1971	AUG. 10, 1971	AUG. 11, 1971	AUG.
2.	Lbs. Limestone Injected	397,400	432,900	72,500	
3.	Limestone Feedrate Lbs/Hr	16,600	18,000	16,700	
4.	Injection Duration	HRS 24 MIN 0	H 24 M 0	H 4 M 20	H
5.	Coal Burned Lbs.	UNIT 9 2,178,500	U9 2,437,500	U9 2,417,500	2
		UNIT 10 2,621,000	U10 2,802,500	U10 2,670,000	
6.	% Sulfur in Coal (Bunker Sample)	1.42	4.40	3.18	
7.	% Sulfur (a) Using Avg. ppm & O_2	2.92	3.12	3.18	
	(b) Assuming 25% EA	2.32	2.52	2.37	
8.	Avg. SO_2 (ppm) in Flue Gas	1800	1960	1840	
9.	Avg. O_2 (%) in Flue Gas	7.4	7.3	8.4	
10.	Gross Generation, kWh	UNIT 9 2,415,000	U9 2,761,000	U9 2,651,000	2
		UNIT 10 2,881,000	U10 2,931,000	U10 2,869,000	2
11.	Net Generation, kWh	UNIT 9 2,260,000	U9 2,596,000	U9 2,489,000	2
		UNIT 10 2,701,000	U10 2,750,000	U10 2,697,000	2
12.	Avg. Load, KW	120,042	122,125	95,000	
13.	Pulverizer, kWh (M3739)	4200	4600	700	
14.	U10 kWh (M3747)	4100	4000	1000	
15.	U9 kWh (M3748)	1100	1000	400	
16.	Fuel Oil Consumed (Gal.)	946	741	216	
17.	Total No. IK's Operated	UNIT 9 30	U9 31	U9 32	
		UNIT 10 46	U10 46	U10 60	
18.	Total No. IR's Operated	UNIT 9 24	U9 12	U9 17	
		UNIT 10 16	U10 30	U10 32	
19.	MECH, Sluice Time UNIT 9	HRS 5 MIN 20	U9-H 2 M 15	U9-H 4 M 40	H
	UNIT 10	HRS 9 MIN 45	U10-H 11 M 19	U10-H 7 M 55	H
20.	ESP, Sluice Time UNIT 9	HRS 1 MIN 10	U9-H 1 M 50	U9-H 1 M 15	H
	UNIT 10	HRS 3 MIN 40	U10-H 0 M 45	U10-H 1 M 30	H
21.	Bottoms, Sluice Time UNIT 9	HRS 2 MIN 20	U9-H 1 M 20	U9-H 2 M 25	H
	UNIT 10	HRS 2 MIN 5	U10-H 2 M 15	U10-H 1 M 40	H
22.	% Lime Utilization (Avg.)	17.27	13.71	16.82	
23.	Stoichiometry * From Linestone Fed * ppm and O_2 in Flue Gas (*Avg. Daily Values)				
	(a) Using Meas. O_2	1.74	1.73	2.05	
	(b) Assuming 25% EA	2.14	2.14	2.74	
24.	% SO_2 Removal From Stoichiometry X % Utilization				
	(a) Using Meas. O_2	30.0	23.7	34.5	
	(b) Assuming 25% EA	37.0	29.3	46.1	

25. % SO_2 Removal From ΣSO_2:

	EAST	WEST	EAST	WEST	EAST	WEST	EAST
11:00 - 7:00 Shift	-	-	-	-	17.7	19.0	
7:00 - 3:00 Shift	-	-	-	-	-	-	
3:00 - 11:00 Shift	-	-	10.2	14.0	-	-	
AVG.	-	-	-	-	-	-	

Table 20

SHAWNEE STEAM PLANT
DRY LIMESTONE PROJECT
LONG TERM INJECTION TESTS

Summary Sheet

Trial 1

AUG. 12, 1971	AUG. 13, 1971	AUG. 14, 1971	AUG. 15, 1971	AUG. 16, 1971	AUG. 17, 1971
NONE	57,300	287,100	218,200	255,500	185,900
	17,625	12,350	9,385	11,125	8,030
H M	H 3 M 15	H 23 M 15	H 23 M 15	H 22 M 58	H 23 M 9
2,262,500	2,587,500	2,251,000	2,969,500	3,020,500	2,179,000
	2,359,000	2,611,000	2,904,000	2,968,500	2,334,000
	No Sample Taken	1.99	4.57	1.29	1.75
	3.94	3.66	2.79	2.85	3.24
	4.07	3.31	2.39	2.73	2.69
	3210	2690	1850	2130	2090
	3.5	5.4	6.0	5.6	7.1
2,505,000	2,679,000	2,557,000	3,208,000	3,251,000	2,551,000
2,342,000	2,371,000	2,779,000	3,113,000	3,211,000	2,545,000
2,351,000	2,514,000	2,394,000	3,019,000	3,064,000	2,396,000
2,192,000	2,218,000	2,600,000	2,924,000	3,018,000	2,384,000
97,583	125,333	115,792	129,708	133,792	106,042
0	0	3600	4900	3400	1500
-	-	2600	3300	3500	2800
-	-	600	600	500	300
0	0	1000	328	444	180
26	24	26	40	40	32
34	30	62	62	81	46
12	8	12	32	28	12
21	8	10	21	27	9
H 3 M 30	H 3 M 10	H 8 M 45	H 8 M 15	H 8 M 25	H 4 M 25
H 8 M 10	H 6 M 25	H 9 M 0	H 6 M 40	H 5 M 50	H 9 M 3
H 0 M 35	H 0 M 25	H 0 M 25	H 1 M 20	H 2 M 0	H 0 M 10
H 7 M 25	H 13 M 50	H 5 M 0	H 3 M 48	H 3 M 15	H 5 M 56
H 2 M 15	H 1 M 15	H 3 M 35	H 2 M 12	H 2 M 58	H 1 M 50
H 2 M 0	H 2 M 15	H 1 M 15	H 2 M 40	H 1 M 50	H 1 M 20
	No Samples Taken	19.62	15.64	15.96	20.39
	1.31	1.06	0.95	1.05	0.85
	1.25	1.18	1.10	1.12	1.03
		20.8	14.86	16.8	17.33
		23.2	17.20	17.9	21.00

EAST	WEST	EAST	WEST	EAST	WEST	EAST	WEST	EAST	WEST	EAST	WEST
				12.7	13.3	19.0	15.3	9.1	8.0	14.3	10.5
				10.8	7.3	7.1	5.0	13.6	10.9	10.2	11.3
				16.1	12.5	5.4	7.1	14.8	15.0	9.7	7.8
				13.2	11.0	10.5	9.1	12.5	11.3	11.4	9.9

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UG. 16, 1971	AUG. 17, 1971	AUG. 18, 1971	AUG. 19, 1971
255,500	185,900	209,600	200,300
11,125	8,030	9,015	11,285
22 M 58	H 23 M 9	H 23 M 15	H 17 M 45
3,020,500	2,179,000	2,449,500	2,394,000
2,968,500	2,334,000	2,382,000	2,402,000
1.29	1.75	3.25	3.84
2.85	3.24	3.27	3.56
2.73	2.69	2.94	3.32
2130	2090	2300	2610
5.6	7.1	5.9	5.5
3,251,000	2,551,000	2,803,000	2,715,000
3,211,000	2,545,000	2,618,000	2,587,000
3,064,000	2,396,000	2,632,000	2,547,000
3,018,000	2,384,000	2,451,000	2,424,000
133,792	106,042	109,083	99,444
3400	1500	400	0
3500	2800	2400	1700
500	300	300	100
444	180	114.9	0
40	32	36	28
81	46	48	44
28	12	17	16
27	9	16	12
8 M 25	H 4 M 25	H 7 M 25	H 5 M 55
5 M 50	H 9 M 3	H 11 M 53	H 8 M 10
2 M 0	H 0 M 10	H 2 M 0	H 1 M 5
3 M 15	H 5 M 56	H 4 M 48	H 3 M 20
2 M 58	H 1 M 50	H 1 M 20	H 2 M 55
1 M 50	H 1 M 20	H 1 M 0	H 1 M 35
15.96	20.39	20.19	19.37

1.05	0.85	0.92	1.18
1.12	1.03	1.02	1.24

16.8	17.33	18.6	22.9
17.9	21.00	20.6	24.0

AST	WEST	EAST	WEST	EAST	WEST	EAST	WEST
9.1	8.0	14.3	10.5	14.5	13.4	-	13.5
3.6	10.9	10.2	11.3	14.8	13.5	-	10.4
4.8	15.0	9.7	7.8	-	9.0	-	-
2.5	11.3	11.4	9.9	14.7	12.0	-	12.0

ITEM NO.	DATE	
	AUGUST 9, 1971	
19	AUGUST 10, 1971	All times
20		All times
19	AUGUST 11, 1971	All times
10		Unit 10 M
12		Avg. Load
19	AUGUST 12, 1971	NOTE: No
19		All times
20		All times
4	AUGUST 13, 1971	Injection
10		Gross Gen (9:00 p
12		Avg. Load
19		All times
19	AUGUST 14, 1971	All times
	AUGUST 15, 1971	
	AUGUST 16, 1971	
19	AUGUST 17, 1971	All times
	AUGUST 18, 1971	
	AUGUST 19, 1971	NOTE: St
10		Gross Gen 12:00 p
12		Avg. Load

ITEM NO.	DATE	REMARKS
	AUGUST 9, 1971	
19	AUGUST 10, 1971	All times not available on Unit 10.
20		All times not available on Unit 10.
19	AUGUST 11, 1971	All times not available on Unit 10.
10		Unit 10 kWh - 475,000 from 12:00 MN until 5:00 a.m.
12		Avg. Load, kW - 95,000 (12:00 p.m. to 5:00 a.m.)
19	AUGUST 12, 1971	NOTE: No stone injected on this day.
19		All times not available on Unit 9.
20		All times not available on Unit 10.
4	AUGUST 13, 1971	Injection Duration (8:45 p.m.-12:00 p.m. - 3 hrs. 15 min.)
10		Gross Generation, kWh, Unit 10, 2,371,000 (9:00 p.m. - 12:00 p.m. - 376,000 kWh)
12		Avg. Load, kW - 125,333 from 9:00 to 12:00 p.m.
19		All times not available on Unit 9.
19	AUGUST 14, 1971	All times not available on Unit 9.
	AUGUST 15, 1971	
	AUGUST 16, 1971	
19	AUGUST 17, 1971	All times not available on Unit 9.
	AUGUST 18, 1971	
	AUGUST 19, 1971	NOTE: Stone off at 6:15 p.m.
10		Gross Generation, kWh Unit 10 (1,790,000 Generated from 12:00 p.m. to 6:00 p.m.)
12		Avg. Load, kW - 99,444 from (12:00 p.m. to 6:00 p.m.)

TRIAL 2

Results of Trial 1 showed that it might be helpful to stabilize ash properties by burning coal from one source. Weeks were required to stockpile this coal and prepare for Trial 2 which got underway January 2, 1972, and lasted until January 9th. Again, the culprit was reheater plugging. Pressure drop, which began at normal level, rose exponentially after about two days. A brief interruption occurred shortly after starting when bunkering of the wrong coal took place. The total injection period lasted only 164 hours and resulted in 836 tons of Fredonia limestone being injected. It was decided to limit the maximum allowable reheater pressure drop to 2" w.c. for Trial 2 with limestone injection. This eliminated the possibility of an outage for cleaning the reheater. The reheater did not plug during Trial 2 test.

The limestone feed rate at 1X stoichiometric plus the uniform coal supply did not yield improved results. Extra effort in cleaning hydroveyors after each sluice cycle did not develop new information beyond confirming the need for keeping their efficiency high to accomplish sluicing at all. Soot blowing also proved its inability to cope with these reheater deposits which reached incipient plugging stage.

Results of Trial 2 are summarized in table 21. Full load was held on the unit and limestone did not exceed the 11,000 lb./hr. goal except on one day. The reheater differential is shown in figure 96. The more specific details covering each of these problem areas is discussed in the following sections.

Reheater Plugging

Utility boilers of significant size often have reheaters to improve steam generator efficiency. Since reheater temperatures are on the order of 1000°F lower than furnace temperatures, most of the heat input to the reheater is by convection. Large tube surface area is required which results in numerous, close-packed tube pendants. Each Shawnee reheater pendant consists of sixteen 2" OD tubes located on 3" centers with only 1" design nominal gas passage, see figure 94. This space is often reduced because tube repairs and cleanings over the years have caused pendants to become warped or misaligned. Restricted spacings favor deposit formation. Sootblowers are located at two elevations upstream of the reheater and at one level downstream, as shown in figure 94. Their operation once a shift normally keeps the reheater clean with a resulting gas side differential of 1.2 to 1.4" W.C. These are long retractable IK blowers whereas IR refers to short retractable blowers that cut slag from selected water wall areas where no effect of limestone injection has been observed.

Reheater plugging reveals itself by (1) rapid or exponential rise in pressure drop that is not reduced by repeated soot blowing and (2) inability to regain or hold reheat steam temperature. Because soot blowing does not relieve the problem, a unit outage is necessary to permit manual cleanup of hard deposits on a row-by-row basis. Observation during numerous inspections shows that random limestone-fly ash deposits are not removed along present sootblower paths and, therefore, installation of additional blowers would be useless.

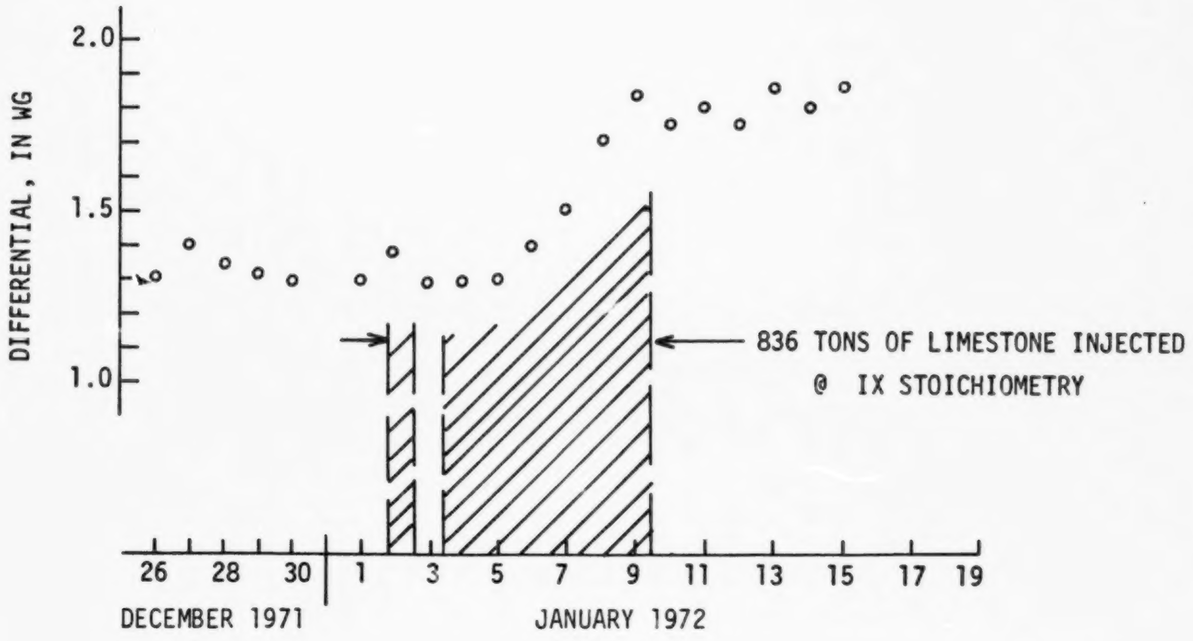
Early in Phase I of the project excessive ash deposits lodged in the reheater and

FIGURE 96

REHEATER DIFFERENTIAL

TRIAL 2, LONG TERM INJECTION

DIFFERENTIALS READ WITHIN ONE HOUR
AFTER BLOWING IK NUMBERS 7,8,9, & 10 AT LOADS
142 - 146 MW ON UNIT 10



ITEM NO.	DESCRIPTION			
1.	For Data Taken (Date)		January 2, 1972	January 3, 1972
2.	Lbs. Limestone Injected		153,454	61,054
3.	Limestone Feedrate Lbs/Hr		10,142	11,809
4.	Injection Duration		HRS 15 MIN 8	H 5 M 10
5.	Coal Burned Lbs.		UNIT 9 3,199,500	U9 2,859,500
			UNIT 10 3,111,000	U10 3,062,500
6.	% Sulfur in Coal (Bunker Sample)		4.09	2.03
7.	% Sulfur (a) Using Avg. ppm & O_2		3.05	2.33
	(b) Assuming 25% EA		3.08	2.43
8A.	Avg. SO_2 (ppm in Flue Gas Actual Reading)		2260	1620
8B.	Avg. SO_2 (ppm) in Flue Gas Assuming 10% removal per unit stoich.)		2410	1890
9.	Avg. O_2 in Flue Gas		3.9	3.4
10.	Gross Generation, kWh		UNIT 9 3,607,000	U9 3,224,000
			UNIT 10 3,434,000	U10 3,350,000
11.	Net Generation, kWh		UNIT 9 3,411,000	U9 3,042,000
			UNIT 10 3,243,000	U10 3,157,000
12.	Avg. Load, kW		143,083	139,583
13.	Pulverizer, kWh (M3739)		0	2100
14.	U10 kWh (M3747)		500	1500
15.	U9 kWh (M3748)		100	600
16.	Fuel Oil Consumed (Gal.)		0	494
17.	Total No. IK's Operated		UNIT 9 26	U9 30
			UNIT 10 68	U10 60
18.	Total No. IR's Operated		UNIT 9 14	U9 8
			UNIT 10 40	U10 40
19.	MECH, Sluice Time	UNIT 9	HRS 4 MIN 45	U9-H 5 M 5
		UNIT 10	HRS 5 MIN 45	U10-H 5 M 35
20.	ESP, Sluice Time	UNIT 9	HRS 2 MIN 37	U9-H 1 M 1
		UNIT 10	HRS 2 MIN 45	U10-H 2 M 20
21.	BOTTOMS, Sluice Time	UNIT 9	HRS 1 MIN 53	U9-H 4 M 8
		UNIT 10	HRS 2 MIN 11	U10-H 1 M 21
22.	% Lime Utilization (Avg.)		14.83	No Samples Taken
23A.	Stoich. *From Bunker Coal S. *Load		0.63	1.45
23B.	Stoich. *From Limestone Fed *ppm & O_2 in Flue Gas *Load (*Avg. Daily Values)			
	(a) Using Meas. O_2		0.85	1.32
	(b) Assuming 25% EA		0.84	1.26
24.	% SO_2 Removal From Stoichiometry X % Utilization			
	(a) Using Meas. O_2		12.6	-
	(b) Assuming 25% EA		12.5	-

Table 21

SHAWNEE STEAM PLANT
DRY LIMESTONE PROJECT
LONG TERM INJECTION TESTS

Summary Sheet

Trial 2

January 3, 1972	January 4, 1972	January 5, 1972	January 6, 1972	January 7, 1972	Januar
61,054	239,369	*256,800	236,327	239,960	2
11,809	9,974	10,700	9,847	9,998	
H 5 M 10	H 24 M 0	H 24 M 0	H 24 M 0	H 24 M 0	H 24
U9 2,859,500	U9 2,989,500	3,180,500	1,865,000	OFF LINE	2,3
U10 3,062,500	U10 2,935,500	2,915,000	2,882,500	2,933,000	2,9
2.03	2.33	1.65	2.22	2.11	
2.33	2.35	2.20	1.83	2.42	
2.43	2.43	2.25	1.84	2.41	
1620	1680	1450	1410	1650	
1890	1890	1740	1590	1870	
3.4	3.6	3.8	4.1	4.3	
U9 3,224,000	U9 3,623,000	3,597,000	2,238,000	OFF LINE	2,5
U10 3,350,000	U10 3,366,000	3,418,000	3,444,000	3,486,000	3,4
U9 3,042,000	U9 3,426,000	3,396,000	2,105,000	OFF LINE	2,3
U10 3,157,000	U10 3,171,000	3,219,000	3,237,000	3,279,000	3,2
139,583	140,250	142.417	143,500	145,250	1
2100	2200	3600	6000	3700	
1500	3200	4900	3600	3800	
600	800	1000	1500	1000	
494	529	709	1198	800	
U9 30	U9 41	50	24	OFF LINE	
U10 60	U10 74	63	67	65	
U9 8	U9 20	13	16	OFF LINE	
U10 40	U10 44	48	50	30	
U9-H 5 M 5	U9-H 3 M 45	H 4 M 30	H 7 M 17	H M	H 3
U10-H 5 M 35	U10-H 8 M 25	H 11 M 33	H 7 M 55	H 8 M 32	H 7
U9-H 1 M 1	U9-H 1 M 45	H 2 M 19	H 1 M 30	H M	H 2
U10-H 2 M 20	U10-H 2 M 55	H 2 M 0	H 1 M 42	H 1 M 58	H 2
U9-H 4 M 8	U9-H 1 M 30	H 1 M 28	H 1 M 33	H M	H 0
U10-H 1 M 21	U10-H 1 M 35	H 0 M 45	H 2 M 50	H 1 M 10	H 2
No Samples Taken	14.82	14.83	16.51	15.29	1
1.45	1.11	1.66	1.14	1.19	
1.32	1.10	1.25	1.37	1.04	
1.26	1.07	1.22	1.36	1.05	
-	16.3	18.5	22.6	15.9	1
-	15.9	18.1	22.5	16.1	1

January 7, 1972	January 8, 1972	January 9, 1972
239,960	239,064	*245,000
9,998	9,961	11,000
H 24 M 0	H 24 M 0	H 22 M 17
OFF LINE	2,304,000	3,194,000
2,933,000	2,985,000	2,921,000
2.11	2.29	2.08
2.42	2.55	2.55
2.41	2.55	2.60
1650	1760	1750
1870	1980	2020
4.3	4.2	3.7
OFF LINE	2,501,000	3,637,000
3,486,000	3,480,000	3,392,000
OFF LINE	2,344,000	3,445,000
3,279,000	3,281,000	3,198,000
145,250	145,000	141,333
3700	2800	2600
3800	3200	3000
1000	800	700
800	604	480
OFF LINE	26	31
65	66	93
OFF LINE	8	36
30	42	32
H M	H 3 M 27	H 3 M 35
H 8 M 32	H 7 M 43	H 10 M 2
H M	H 2 M 13	H 2 M 0
H 1 M 58	H 2 M 30	H 2 M 30
H M	H 0 M 50	H 1 M 55
H 1 M 10	H 2 M 12	H 1 M 38
15.29	14.83	15.39
1.19	1.09	1.35
1.04	0.98	1.12
1.05	0.98	1.10
15.9	14.5	17.2
16.1	14.5	16.9

January 5, 1972 - Item No. 2, *Estimated,

January 7, 1972 - Unit 9 Off Line

January 9, 1972 - Item No. 2, *Estimated,

ry 9, 1972
245,000
11,000
M 17
194,000
921,000
2.08
2.55
2.60

1750

2020
3.7
637,000
392,000
445,000
198,000
141,333
2600
3000
700
480
31
93
36
32
M 35
M 2
M 0
M 30
M 55
M 38
15.39
1.35

1.12
1.10

17.2
16.9

January 5, 1972 - Item No. 2, *Estimated, Chart Readings Not Accurate

January 7, 1972 - Unit 9 Off Line

January 9, 1972 - Item No. 2, *Estimated, Chart Readings Not Accurate resulted in a boiler outage. Significant quantities of limestone were injected beginning in February 1970. Between February 1 and May 8 the pressure drop (PD) gradually increased from 1.6 to 2.0 inches and on May 9 the pressure drop was 2.5 inches, rising ultimately by May 14 to 6.0 inches when the unit came down for reheater cleaning. A total of 592 tons of limestone had been injected. Soot blowing had not been increased until the PD reached 3 inches.

After this cleaning the PD ranged between 1.3 and 1.6 inches during the period May 18 and June 9. The slight increase was deceptive because inspection on June 9 (a tube leak caused a forced outage) revealed a heavy buildup of deposits although only 322 tons of limestone had been injected. The reheater was cleaned again and the PD ranged from 1.2 to 1.5 inches until September 12 when the unit came off for annual maintenance outage. The reheater inspection revealed only isolated patches of deposit and overall was very clean. Between June 10 and September 12, 1970, a total of 1,323 tons of limestone was injected with the bulk of it injected after July 16.

Differences in the coal burned were postulated as cause of the plugging problem but analysis of the coal ash composition, ash fusion temperatures, and sulfur forms failed to reveal any significant differences. Results of analyses on these samples from Phase I are given in table 22. A review of reheater PD did not indicate impending plugging until it was too late to attempt recovery by increased soot blowing (see table 23).

Reheater tube deposits were analyzed from two independent viewpoints. Babcock & Wilcox analyzed data from the aspect of how limestone addition would affect slagging characteristics of the modified fly ash. The second approach was a petrographic and mineralogical analysis carried out by Dr. R. D. Harvey as part of his larger study[17] on limestone. Data from the May and June 1970 coal ash analyses showed these coals to have "medium fouling" tendencies without additive and, as such, should not produce any special reheater plugging problem. Babcock & Wilcox also concluded that a medium-fouling coal ash plus limestone additive could develop high sintering strengths through sulfation bonding (interlocking $CaCO_4$ crystals) if soft deposits were allowed to remain in place on reheater surfaces for a period of several days. The coals were predicted to have ash with medium slagging characteristics when limestone was not injected. Also, similar temperatures for a calculated viscosity property would not be expected to contribute to severe deposition problems in the reheater. The reheater deposit analysis falls in a "low fouling" classification. A correlation was found between low average additive feed rates and reheater plugging when limestone was injected intermittently. The intermittent injection allows deposit composition to swing back and forth through a minimum ash fusion temperature range and this could increase slagging and fouling problems. Coal ash analysis (table 22) shows 6% CaO content whereas the reheater deposits show an outer layer of 41% for samples obtained during the September 1971 outage.

Detailed chemical and mineral analyses showed minor differences between inner and outer layers both of which consisted largely of anhydrite mixed with less abundant normal fly ash particles. Sintering and interlocking growth textures of anhydrite grains

Table 22

CHEMICAL ANALYSES OF COAL ASH, COAL SULFUR FORMS AND REHEATER DEPOSIT

	May 12, 1970	May 19, 1970	June 2, 1970
Coal Ash Analysis			
SiO_2, %	45.4	48.0	47.4
Al_2O_3	19.8	20.0	20.3
Fe_2O_3	17.6	12.5	14.7
CaO	5.6	6.1	5.7
MgO	1.1	1.1	1.1
SO_2	4.7	5.1	2.8
Na_2O	0.7	1.1	0.9
K_2O	2.1	2.1	2.1
Sulfur Forms			
Sulfate Sulfur, %	0.18	0.06	0.08
Pyritic Sulfur	1.46	1.17	1.27
Organic Sulfur	1.18	0.86	0.74
Total Sulfur	2.82	2.09	2.09
Ash Fusion Temperature, °F			
Oxidizing Atmos.			
ID	2,320	2,310	2,310
HT	2,370	2,360	2,360
FT	2,380	2,370	2,380
Reducing Atmos.			
ID	2,050	2,100	2,060
HT	2,130	2,210	2,130
FT	2,170	2,260	2,180

Deposit taken from reheater

SiO_2	19.0%	MgO	0.5%
Al_2O_3	9.2	SO_3	34.2
Fe_2O_3	6.7	Na_2O	0.6
CaO	25.0	K_2O	1.0

Table 23

REHEATER DIFFERENTIAL, SOOTBLOWING CYCLES AND LIMESTONE INJECTION DATA

Date	Reheater Diff. "w.g. East	Reheater Diff. "w.g. West	No. of 1K Soot Blows Per Day (@ 150 PSIG)	Limestone Injected Tons/Day
1970				
6-1	1.5	1.3	40	
6-15	1.5	1.3	28	
6-30	1.6	1.4	28	
7-1	1.6	1.4	34	
7-15	1.6	1.4	29	
7-30	1.5	1.3	22	
8-1	1.6	1.4	16	
8-15	1.6	1.4	32	
8-30	1.7	1.5	38	
9-1	Unit Off			
9-5	1.7	1.5	14	
9-15	1.6	1.4	16	
9-30	1.6	1.4	18	
10-1	1.7	1.5	30	50 (10-3)
10-15	1.6	1.4	48	
10-30	1.6	1.4	52	
11-1	1.6	1.4	40	
11-15	1.6	1.4	39	
11-24	1.24	1.26		45
11-25	1.24	1.27		22
12-2	1.28	1.28		14
12-3	1.30	1.30		43
12-4	1.26	1.26		48
12-8	1.44	1.41		31
12-10	1.30	1.30		38
12-11	-	-	36	30
12-15	1.35	1.36		38
12-16	1.24	1.26		35
12-30	1.29	1.30	27	44

Date	Reheater Diff. "w.g. East	Reheater Diff. "w.g. West	No. of 1K Soot Blows Per Day (@ 150 PSIG)	Limestone Injected Tons/Day
1971				
1-5	1.37	1.40		23
1-7	1.38	1.40		31
2-9	1.45	1.36		36
2-11	1.48	1.33		22
2-16	1.45	1.30		24
2-26	1.46	1.35		12
3-2	1.50	1.40		5
3-3	1.55	1.46		33
3-4	1.51	1.40		16
3-5	1.50	1.36		22
4-1	1.60	1.46	37	15
4-2	1.57	1.42		28
4-5	1.60	1.40		29
4-6	1.60	1.40		11
4-7	1.55	1.47		23
4-8	1.58	1.43		14
4-9	1.60	1.50		42
4-12	1.71	1.63		30
4-13	1.71	1.58		22
4-14	1.79	1.53		22
4-15	1.74	1.64	51	3
4-16	1.80	1.70		26
4-20	1.84	1.71		15
4-21	2.04	1.86		3
4-22	2.07	1.92		14
4-23	2.00	1.83		20
4-26	2.11	1.85		25
4-27	-	-		8
4-28	2.03	1.85		24
4-29	2.10	1.94		18

Table 23 (Continued)

Date	Reheater Diff. "w.g. East	Reheater Diff. "w.g. West	No. of 1K Soot Blows Per Day (@ 150 PSIG)	Limestone Injected Tons/Day
1971				
5-4	2.29	2.11	38	29
5-5	2.41	2.17	48	16
5-6	2.53	2.24	48	9
5-7	2.50	2.28	40	24
5-10	2.56	2.29	32	18
5-11	2.60	2.35	38	20
5-12	-	-	42	17
5-13	2.80	2.50	66	18
5-14	2.40	2.20	78	10
5-15	Unit Off			
5-20	1.26	1.15	56	9
5-21	1.21	1.11	40	18
5-24	-	-	50	20
5-25	-	-	52	14
5-26	-	-	54	11
5-27	-	-	58	27
5-28	-	-	36	16
6-3	1.35	1.20	36	13
6-4	1.31	1.20	62	14
6-7	1.37	1.26	48	17
6-8	1.40	1.30	36	13
6-9	1.35	1.20	52	16
6-10	-	-	48	9
6-11	-	-		35
6-15	1.50	1.30	17	12
6-23	1.45	1.30		4
6-24	1.44	1.31		39
6-25	1.43	1.31		8
6-28	1.26	1.16		27
6-29	-	-		29
1971				
7-10	1.40	1.25		27
7-12	1.60	1.30		23
7-13	1.50	1.35		14
7-14	-	-		13
7-15	-	-	52	36
7-19	1.50	1.30		14
7-20	1.65	1.40		10
7-21	1.42	1.30		11
7-22	-	-	28	22
7-23	-	-		21
7-24	1.60	1.40		35
7-26	1.60	1.45		26
7-27	1.60	1.40		12
7-28	1.60	1.40	24	9
8-9	1.60	1.50		199
8.10	1.58	1.43		216
8-11	-	-	32	36
8-13	1.68	1.48	24	29
8-14	1.66	1.47		144
8-15	1.81	1.65		109
8-16	1.83	1.67		128
8-17	1.91	1.77		93
8-18	2.04	1.88	28	105
8-19	2.03	1.82	28	100

were observed in the largest and hardest deposits. The mean concentrations of K_2O and Na_2O of the layer adjacent to the tube surface were higher than those in the outer layer. A coal ash deposition study[18] showed (statistically) sodium having the greatest influence on strength of any single constituent. Perhaps the interaction of these constituents or changes in deposited material with time accentuated the plugging in the Shawnee reheater. Then again, the physical increase in dust loading may have been the major factor.

The Babcock & Wilcox report[19] recommended (1) maintaining a high soot blowing frequency and (2) eliminating intermittent or periodic limestone injection. B&W stated that if additives are injected, a constant and high additive injection rate should be used. The first recommendation was followed but the second was incompatible with program requirements until Phase IV.

Soot blowing had increased 25% in Phase I and is tabulated in table 23. During Phase IV, for the period August 7 to September 7, 1971, the total number of blowing cycles for the four IK blowers 7, 8, 9, and 10, all located ahead of the reheater, was 190 for Unit 9 (without limestone injection) and 370 for Unit 10 or nearly twice the soot blowing in this region. Inspections indicated that deposition patterns were random. Soot blowers appeared to have rather limited coverage in removing limestone-fly ash deposits on the reheater, being most effective in an area 3 feet above and below blower elevation. No additional blowers were installed for the test program. It appeared that some deposits dislodged from the front rows of the reheater were caught again in rear rows thus abetting plugging. Long trailing edge deposits up to 4 inches were easily knocked off by hand lance when checked for hardness.

The reheater plugging usually was concentrated in the first four to six rows of tubes. This location could conceivably shift to more forward pendants when gas temperature and velocity, probably both important in deposit formation, are reduced under low load operation. But the secondary superheater has much greater tube spacing so plugging due to limestone might not arise there.

Experience at other limestone injection facilities shows that plugging has occurred in portions of tne reheater where even 7" tube spacing exists but where additional soot blowers reportedly helped. The same plant reported plugging in first and second banks of horizontal, low temperature superheaters where space between tubes was 1-1/2". A second plant reported no problems in the high temperature superheater or the reheater probably because of wide tube spacing. Plugging occurred in the primary SH and economizer first banks in addition to plugging in hoppers serving a tubular air heater. The tube deposits were hard and required high pressure water jets for removal. A third plant in which both dolomite and limestone injection test programs were conducted also experienced plugging in the primary superheater and reheater tube bundles. Long stalactite deposits (18") formed on downstream surfaces of these horizontal elements.

They were hard surfaced and yellowish-orange in color but had powdery gray-white interior material. Chemical analysis indicated these deposits were predominantly calcium sulfate, calcium and magnesium oxides. Reheater tube spacing varied in three stages with the closest at 2 inches between tubes, the same as in primary superheater and economizer. The personnel believed that properly installed sootblowers would control these deposits. This was based on trial sootblower installed within the 2nd and 3rd reheater banks.

Direct comparison of the above experience with that at Shawnee may not extend beyond comparable gas temperatures and deposit analyses. None have the close tube spacing of the Shawnee reheater which undoubtedly accelerates plugging under injection conditions. The effect of stoichiometry alone shows that low injection rate of 1X, as used in Trial 2, did not delay the rate of buildup any more than did 2X stoichiometric injection.

Hydroveyor Plugging

The second major handicap to long-term operation was deposition of modified limestone-fly ash mixture in the throat and combining tube of hydroveyors. Two hydroveyors were involved, one that serves the precipitator sluice line and the other on the combined pyrites and mechanical fly ash hoppers sluice line.

Normal fly ash usually gives trouble-free operation but addition of the cementitious CaO and sulfated calcium material created problems. A wet-dry interface exists at the hydroveyor inlet which, as buildup occurs, is moved even further upstream where flow area was greatly reduced. Reductions of 60-70% of diameter were observed. Limestone-fly ash mixture even encircled the jets requiring them to tunnel through the deposit with serious loss of aspirating action. A section view is shown in figure 97 and a photo of the deposit in figure 98. This reduced the solids removal capacity and lengthened sluicing time. Hydroveyor inspection and hand cleaning as necessary after each sluice cycle became part of the operating procedure later in Trial 1 and all during Trial 2. Hardening of the deposit was accelerated because of material temperatures and chemical reactions.

Samples taken from the mechanical hydroveyors were analyzed by Arthur D. Little, Inc., by X-ray fluorescence, optical emission spectroscopy, and X-ray diffraction analysis. Their results by the first two methods showed good agreement with high concentrations of calcium. Optical emission showed 3-30% of calcium and iron present while X-ray diffraction revealed 50-70% Portlandite $Ca(OH)_2$ and 10-20% Ettringite $Al_2O_3 \cdot 3\ CaO \cdot 3\ CaSO_4 \cdot 31\ H_2O$. Table 24 covers their complete analysis but it alone cannot answer the question of whether the modified limestone-fly ash mixture is more cementitious than fly ash alone. Physical examination of samples, taken from hydroveyors immediately after a sluice cycle exhibited rising temperature as a result of chemical reaction or setting activity.

FIGURE 97

HYDROVEYOR

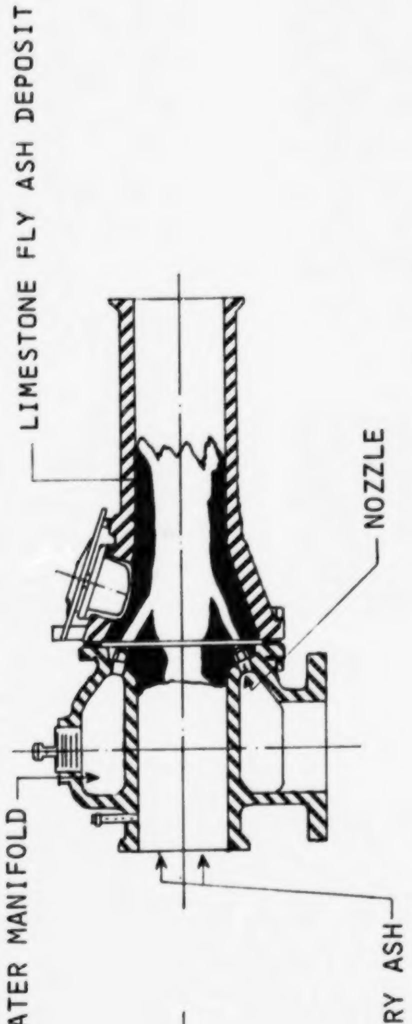
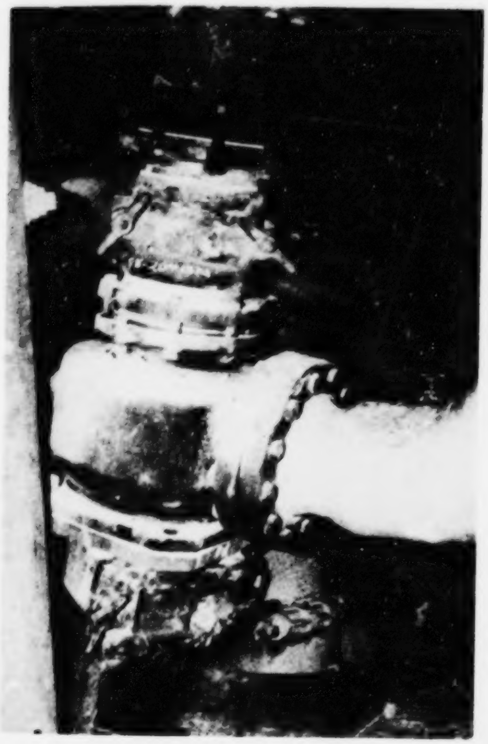
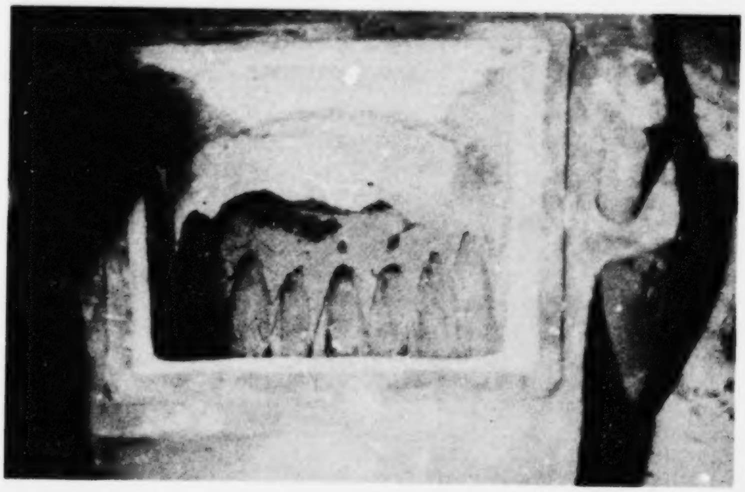

LIMESTONE FLY ASH DEPOSIT
NOZZLE
WATER MANIFOLD
DRY ASH

FIGURE 98



Hydroveyor on electrostatic precipitator hopper sluice line. Located at front of Unit 10.

Hydroveyor on mechanical collector hopper sluice line. Located at front of Unit 10.



Typical limestone fly ash deposit in hydroveyors during long-term injection. Mechanical shown here.

Table 24
HYDROVEYOR DEPOSIT CHEMICAL ANALYSIS BY A.D. LITTLE, INC.

Sample source weight: 83 grams
Sample weight use in analyses: 1 gram
Sample description: exhibited a dull, powdery, light gray surface

X-ray Fluorescence Analysis

The entire sample was pulverized in an agate morter and pestle. This powder was analyzed qualitatively by X-ray fluorescence analysis, yielding the following results:

	Elements
Very strong	Ca
Medium	S
Weak	K, Fe, Al, Si, Ti, Sr
Trace	Rb, Br, Zn

Optical Emission Spectroscopy

A 10 mg sample was arced, yielding the following analysis

Percent Detected	Element
3-30%	Ca, Fe
1-10	Al, Si
0.1-1.0	K, Mg, Ti
0.003-0.03	Ba, Na, Sr
0.001-0.01	B, Mn, Nb, Zn
0.0003-0.003	Cr, Li, Ni, Zr
0.0001-0.001	Cu, Mo
0.00001-0.0001	Co, Pb, Be

These results are in good agreement with the results of X-ray fluorescence.

X-ray Diffraction Analysis

About half of the sample was mixed with a parlodian-in-amyl acetate solution (as a binder) and poured onto a glass microscope slide. An X-ray diffractometer scan was obtained with monochromated CuK$_\alpha$ radiation. The following phases were detected:

Table 24 (continued)

50-70% Portlandite - Ca $(OH)_2$ –
10-20% Ettringite - $Al_2O_3 \cdot 3CaO \cdot 3CaSO_4 \cdot 31H_2O$ –
∿ 5% Calcite - $CaCO_3$ –
∿ 5% Gypsum - $CaSO_4 \cdot 2H_2O$
∿ 5% α-Quartz - SiO_2
∿ 5% Anhydrous $CaSO_4$ (water soluble)
∿ 5% CaO_2

The diffraction analysis is consistent with the elemental analyses reported above.

An attempt to reduce depositions was made with surface coating epoxy. Although hydroveyors are constructed of very hard, high glass content material to resist erosion it was postulated that a smooth surface might reduce the rate of deposit growth. Even short term relief would help the program. The entire length of two new hydroveyors was painted with three coats of epoxy. There was a marginal improvement and some change of deposit pattern but coatings did not yield any significant benefits during the trial and were worn away from impact areas in a week. Raising water pressure above the normal 150 psig somewhat restores efficiency (with normal fly ash) but also increases water consumption and wear. Increasing the water/ash ratio, therefore, develops its own problems. A special test program would probably be required to learn if some modification to existing designs would either reduce rate of buildup or permit on-stream cleanout other than manual. Results at Shawnee showed that limestone-fly ash material generated in amounts considered normal for process application caused hydroveyor pluggage which protracted sluice periods and required manual cleanout.

Additional Coal Requirement

Limestone injection affects boiler efficiency by imposing an incremental heat burden on the boiler cycle. Thermodynamic calculations of the thermal effect and the additional heat requirement are discussed in appendix H for three sulfur levels in coal: 0.8%, 3%, and 5%. Boiler heat is lost during the process steps: $CaCO_3$ calcination, sensible heat loss of inert limestone impurities, and enthalpy changes of liquid water. A small portion of the heat is regained during the exothermic conversion from calcium oxide to calcium sulfate.

Calculations give the following results for a 150 MW unit when burning 12,000 Btu per pound coal:

Base Case	%S in Coal	Limestone Stoichiometry	Additional Coal, lb/hr	Total Coal Requirement lb/hr	lb/kWh
1	0.8	5	874	117,874	.786
2	3.0	2	1127	118,127	.788
3	5.0	2	1901	118,901	.793

The incremental coal percentages for these three cases are 0.75, 0.97, and 1.62, respectively. The thermal effect is primarily a theoretical consideration. In actual boiler operation these small coal increments are within levels of variation experienced due to changes in coal sulfur, moisture, ash and heat content plus slagging effects. During the project period the boiler operators on Shawnee Unit 10 did not detect the added heat burden when limestone was being injected to the furnace. Nevertheless, more coal is burned with attendant incremental consequences of coal handling through final ash disposal. This aspect of the process is fully considered in the section on Process Economics, Appendix L.

Injection Effects on Air Preheater

Unit 10 is equipped with two regenerative-type air preheaters. Each contains 66" of basket height arranged 12, 42, 12. When these units were inspected on October 14, 1971, nearly two months after Trial 1 ended, there was no evidence of permanent type deposit on the heat transfer surfaces. The deposit coloration was lighter than usual, probably because of the limestone. Control room temperature recorders showed that shortly after starting limestone injection the exit flue gas temperature increased 5-10 °F in several minutes and was probably due to limestone dust deposits which may subsequently have been swept away by preheated air.

Dry limestone injection did not appear to adversely affect air preheater operation. The differential did not significantly change during Phase IV, as shown graphically in figure 99 for Trial 1 injection period. The cold end section which normally is a victim of corrosion could not be evaluated in this test but some authorities indicate that a benefit should accrue from limestone injection due to reduced corrosion. Counteracting and probably outweighing this would be the increased erosion on the hot gas inlet end due to higher dust loadings.

Injection Effects on Mechanical Collectors

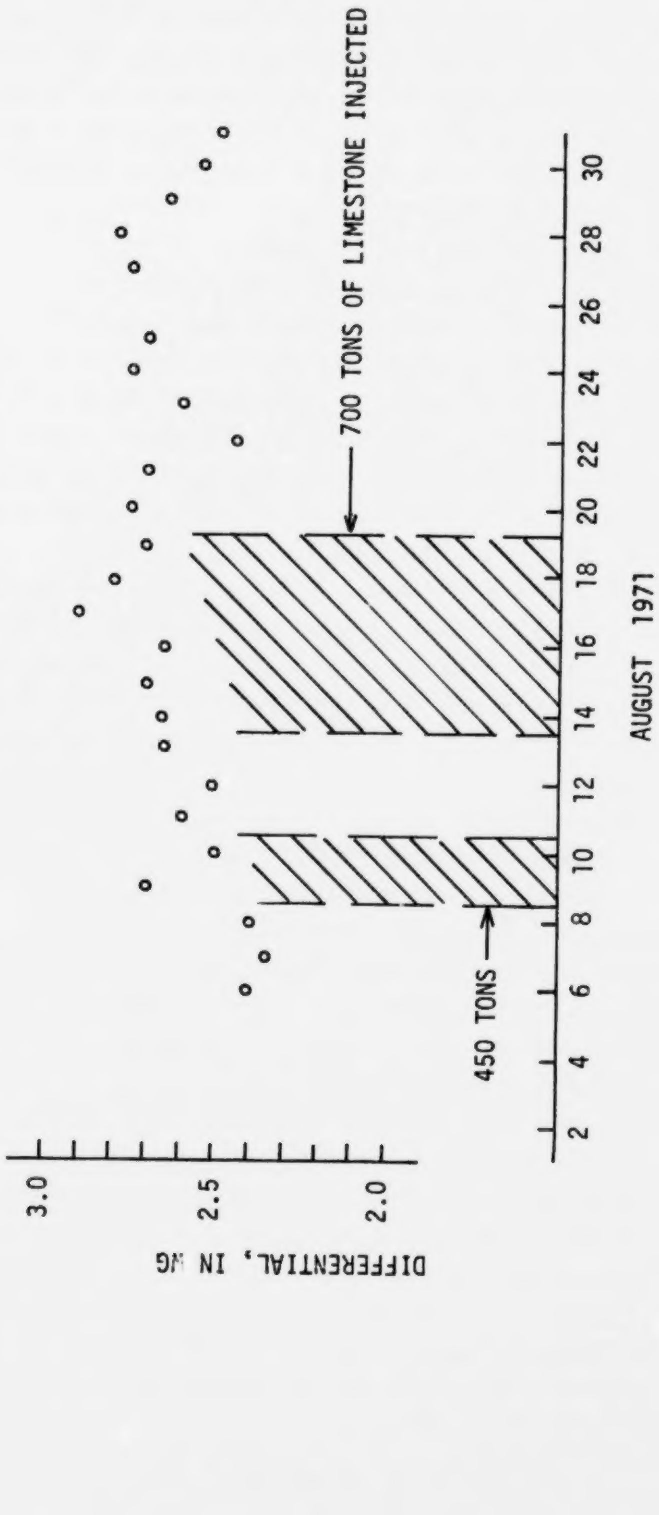
The effects of limestone injection on these collectors were determined in a separate study by Cottrell Environmental Systems and is part of their report which is fully covered in appendix F. During the outage of October 14, 1971, the collectors were inspected but did not reveal any erosion attributable to limestone injection. There were no unusual deposits.

System Operating Reliability

Discussion on system or equipment reliability must follow from recognition that the Dry Limestone Project was designed (1) to serve the expected needs of a test program where operating flexibility was possible and (2) to serve as a full-scale demonstration of the type of equipment required for continuous limestone injection with on-site stone handling and preparation. Equipment was used periodically as determined by the test program. At the conclusion of the project a total of 8,500 tons of raw limestone had been processed with an estimated 7,600 tons actually injected into Unit 10, miniscule amounts in comparison with tonnages handled yearly in coal pulverizers or rock quarry

FIGURE 99

AIR PREHEATER DIFFERENTIAL
TRIAL 1, LONG TERM INJECTION
UNIT 10 LOAD RANGE 135-139 MW



equipment. For this reason, the results with the use of this typical equipment installed at Shawnee cannot reflect long-term continuous service conditions. The only major modification to the system concerned limestone transport piping inside the powerhouse and is discussed below.

Stone Preparation System (refer to figure 6)

Stone was delivered by truck, most often directly dumped into an unloader hopper, but a stockpile was built adjacent to a rail unloading facility that ultimately received only a few loads. This yard proved adequate for project requirements in terms of capacity and foundation. The truck unloader hopper was elevated a couple feet above road elevation resulting in unfavorable dumping angle for semi-trailers. The short conveyor under the hopper was hampered in freezing weather by accumulations of stone behind skirts causing it to impede rotation. The inclined conveyor to the receiving hopper required installation of additional belt scrappers to remove stone build up on large diameter counterweight rollers. Originally, the receiving hopper was uncovered but heavy rain drained onto the dryer belt feeder. A corrugated metal roof was added to the receiving hopper and also reduced heat loss from stone. Freezing weather created extra work in getting stone to feed from the hopper just as it caused delivery trucks to crust over and make dumping troublesome. Nominal minus 1-1/2-inch stone with considerable fines probably aggravated the situation.

There were problems getting proper adjustments on the oil-fired burner for the rotary dryer. Repairs were made on burner refractory where cracks had permitted forced draft to distort flame pattern and cause firing problems. Refractory repairs were also made in the transition piece between burner outlet and dryer inlet. There was a failure of the lower sprocket shaft on the bucket elevator. A new shaft was fabricated at Shawnee and provided satisfactory service after a thorough checkout of alignment.

The dried limestone transported to the surge tank experienced occasional wintertime holdups even though a steep cone angle existed. Condensation entering this closed tank via aspiration cycles of changing stone levels caused half-inch thick deposits to form on the side wall. Sometimes these deposits fell off and contributed to stoppages.

Operation of the ball mill was satisfactory during the test program. Minor feedthrough problems arose now and then which may have been caused by a sound monitor on feed control. The gyrotor classifier nearly experienced a failure when motor current surges revealed some unbalance. A check of this problem showed that bolts supporting the whizzer blade had sheared and would have dropped the whizzer had the problem gone undetected. The use of a grinding system that involved circulating air at sub-atmospheric pressure resulted in an essentially dust-free operation for the limestone processing and handling equipment. This is important where limestone deposition on electrical switchgear could be troublesome. Generally, the storage tank was kept at low levels during phases I, II, and III. Even in phase IV when this tank was full with 275 tons of coarse grind there was no trouble with flow to the transport pump. High material dryness and steep hopper cone angle undoubtedly helped reduce holdups to a minimum. Likewise, operation of the transport pump was troublefree.

In summary, the stone preparation equipment located outside the powerhouse proved adequate mechanically but the sharp drop in grinding capacity when making fine particle size material did require the change to coarse grind for use in Trial 2, Long-Term Injection.

Limestone Injection Equipment

The original system used two equal sized air compressors. The transport compressor would supply air for carrying pulverized limestone to both front and rear injection nozzles but this did not work properly because it lacked control. As one line became overloaded with limestone the pressure dropped and air diverted to the other line. To correct this situation the system was modified by installation of an air receiver and separate transport lines to both front and rear injection distributors as shown in figure 6.

A vexing and time consuming problem concerned shear pin failure in limestone feeder drives. Counter rotating screw feeders discharge their output to a rotary air lock feeder located in each transport line. A chain drives the feeders and air lock so that if stone should not be discharged from the rotary feeder momentarily then the screws lack space to discharge their output. Consequently, this increased screw feeder discharge resistance to the point where drive shear pins failed. The supplier advised increasing pin size which reduced the failure frequency. Static head of limestone appeared to influence feed rate particularly at low tank levels. Air pads in each tank discharge leg assisted the flow. Designwise, use of the screw conveyors appears to be redundant because the rotary air lock is ultimately the feed rate device.

The limestone distributors located at the front and rear of the boiler provided equalized flow to the particular injection lines in service, viz, upper or lower rear and front. Each line was operated with valve full open as it was not possible to monitor two-phase flow at all times. On several occasions the limestone transport piping between the feed tank and the distributors had to be broken at joints or have short sections removed to unplug limestone accumulations that resulted from operating upsets. High-pressure air did not unplug lines.

The need to insert and remove injection nozzles required the use of flexible hoses between transport piping and 3-foot long nozzles. Hose normally used for sandblasting operations failed by erosion at points where the limestone impinged on curved sections. For the long-term injection, the piping was revised as shown in figure 63, to eliminate curved hose sections and have only about 18" of straight hose to care for boiler expansion. Victaulic coupling provided disconnect capability.

Injection nozzles of thick wall stainless steel were used. Inserted shortly before starting injection, these nozzles were cooled by transport air and gave troublefree service. Straight nozzles need only project 3 to 4 inches inside the water wall to overcome influence from wall slag.

Use of separate injection air just before the injection nozzle for purposes of boosting final velocity did not operate as planned. Even with oblique confluence of 45 degrees between the dust conveying transport air and the clean injection air, flow upsets occurred and there was poor control over relative pressure levels in a given transport line. Only transport air flow should be considered as the total injection air source.

Erosion/Corrosion

Dry limestone injection was expected to increase metal erosion in unit 10. Preparations were made to evaluate this during a scheduled outage, December 27, 1968, to January 31, 1969, when tube shields were installed at selected locations on primary and secondary superheaters and on the reheater. Tube diameters were also measured. Intuitively, it was expected that long-term use of limestone injection would increase erosion. The intermittent injection periods during the first three phases of this project and the brief Phase IV precluded any meaningful evaluation of erosion or corrosion. Presumably any increase in erosion would follow the same general pattern that exists for fly ash alone. The 7,600 tons injected during the test program, if it were injected at 2X stoichiometric into a full-load boiler, the additional solids loading would be equivalent to about 38 days of fly ash erosion. This assumes equivalent particle erosive characteristics for the reaction products and fly ash.

Tube shields could not possibly be measured to yield useful data. Likewise, no quantitative data was obtained on changes in corrosion rates that resulted from limestone injection. Removal of some SO_2 and the presence of copious alkaline stone would probably reduce corrosion effects.

Operating Costs for Limestone Injection

The cost data obtained during the test program has been factored into the information found in Appendix L on Process Economics.

Long-term Removal of SO_2

Process SO_2 removal efficiency was determined in previous phases, thus its subordinate position among the objectives of Phase IV. It was not expected that SO_2 removal would be much different than during shorter injection periods. Removal rates were calculated in two ways: First, by measurement of limestone utilization times the stoichiometry and, secondly, by readings from UV analyzers only. Procedural changes in Trial 2 prevented use of UV readings so that results include only the first method.

Results of Trial 1 are summarized in table 20. Based on limestone utilization data and 25% excess air (assumed) the average SO_2 removal per unit stoichiometry was 18.5% for the period August 14-19, whereas, based on UV readings the value was 10.4%. The average SO_2 level was 2411 ppm while burning unspecified source coal.

The results of Trial 2 are summarized in table 21. The SO_2 removal per unit stoichiometry averaged 14.7% for the period January 2-9 when based on utilization data. The SO_2 concentration was 1924 ppm. during the period which also included burning single source coal.

Slightly lower removal during Trial 2 might have been caused by lower SO_2 concentration, the percentage drop being about 20% both in removal and in concentration in comparison to Trial 1. Since limestone injection is a continuous flow process there is no reason to feel that material residence time was different during long-term injection than during other phases.

4. CONCLUSIONS

The Phase IV major goal of long-term operation was not achieved because of reheater plugging and, consequently, other objectives could not be met. The following sections cover conclusions drawn from this limited but revealing evidence regarding dry limestone injection applied to a full-size boiler.

a. Reheater and Hydroveyor Plugging

Limestone injection at 2X and even 1X stoichiometric proved capable of plugging Unit 10 reheater. Doubling the sootblower frequency did not strongly influence deposit formation nor did it help to remove deposits once formed. Deposited slag may actually have been removed and thrust to lodging sites further back in the reheater. Additional sootblowers would probably not have changed the results. In the main, limestone injection experience of other utilities is equivalent to that of Shawnee. In fact, a major supplier of lime/limestone desulfurization systems is no longer promoting boiler injection as a viable mode for flue gas desulfurization.

The narrow gas passages in the reheater (nominal 1") augmented the rate of slag deposit formation and prevented loosened slag from being swept out of the section, the deposits being comparatively cool and not sticky. Gas temperatures in the reheater are below those of the sulfation reaction and far below the vitrification temperature of deadburning, yet the slag showed much higher than usual percentages of CaO and SO_3 than without limestone injection.

Results of Trial 1 @ 2X stoichiometric initially might have set the stage for final plugging after reducing the rate to 1X. However, equally poor results were obtained in Trial 2 @ 1X from the beginning. Injection rate alone does not appear to be the cause.

Resorting to single source coal (Old Ben mines 24 and 26) did not help Trial 2 as compared to use of multi-source coal in Trial 1. Ash content for Old Ben normally ranges from 13.0-17.8%, lower than possible ash content of other coals burned during tests. Ash quality (properties) rather than quantity probably has greater influence on plugging. The specification of coals with narrow ranges of sulfur and ash content in order to accommodate dry limestone injection for SO_2 removal would be very difficult.

Reheater pendant spacing on Unit 10 appears as a critical dimension. (Other investigators found other critical locations.) Removing alternate pendant sections might help but proof of benefits derived would be needed first. Long-term injection at low load might show the effects of lower gas temperature on limestone fortified slag formation but this was not demonstrated here.

Limited injection periods with marl and aragonite preclude any real comparison with the Fredonia, coarse grind, used in Phase IV as to plugging characteristics. Effect of particle size, per se, is unknown but it probably is of no great influence in altering slag fusion properties.

Hydroveyor plugging was caused by limestone modified fly ash which has more cementitious properties than ordinary fly ash. Attempts at smooth surface coating did not help. Increased flushing frequency because of the greater load required more water but did not correct the trouble spot at the wet-dry interface. Hydroveyor modification was not part of this program but solution to this plugging problem would be required to restore pumping capacity. An intermittent blast of high pressure water upstream of the interface to break the throat deposit might be one approach.

b. Boiler Efficiency

Limestone injection affects unit efficiency slightly, due to more sootblowing and sluicing and incremental amounts of coal for the limestone calcination. Excessive tube deposits would reduce heat transfer at designed heat input locations. Energy input to operate the entire injection system is chargeable to station service accounts.

c. Solids Collection

Limestone injection reduces precipitator efficiency but has less effect on mechanical collectors. The extensive test program conducted by Cottrell Environmental Systems at Shawnee quantified the effects of limestone injection on the precipitator and the requirements to maintain a given solids collection efficiency after limestone injection is added to a given boiler. The demonstrated reduction in precipitator efficiency as a result of dry limestone injection and the capital costs associated with upgrading precipitators to maintain a preinjection level of efficiency are both serious drawbacks to the process. Appendix F covers the entire matter of "Limestone Injection Effects on Solids Collection System."

d. Disposal Water Quality

The burdens that limestone injection imposes on the sluice system and disposal water quality have been reviewed. The reader is referred to appendix G where this complex problem is covered and data presented that reveal the severity of increases in most of the ash pond species.

e. Equipment Performance

Limestone preparation and injection equipment proved adequate as to type and general arrangement. Limited use and some test conditions resulted in revisions and there was need for more mill grinding capacity at times. Different boiler types would have their own requirements but they need not differ much from Shawnee. Further design improvements, such as elimination of screw conveyors under the limestone feed tank (figure 6), could be considered.

Erosion would undoubtedly increase in those areas now subjected to fly ash wear alone. Compensatory savings from reduced corrosion are probably unaccountable.

f. Long Term SO_2 Removal

Long term limestone injection ought to achieve SO_2 removal at rates depending on load, stoichiometry, particle size, stone type, etc., and would probably vary only as these factors varied. There is no evidence that indicates SO_2 removal would improve with time.

g. Other Boiler Types

The Shawnee full-scale test program involved only one dry-bottom furnace, the major type found in central station service. The results obtained from this program are applicable to the technology of limestone injection and the specific results obtained will be influenced by numerous factors. One such factor is boiler type. The second major utility boiler type is the slag tap or so-called wet bottom furnace. The original project planning called for full-scale demonstration on both dry bottom and wet bottom types but since the funding was not available for the latter, test data on effects is lacking. However, a review of solids distribution in a wet bottom furnace points out the heavy burden that could come about if dry limestone were injected to this type of furnace.

The ratio of fly ash to bottom ash or slag is quite different in these boilers and thus limestone injection would alter particulate loadings considerably. Pulverized fuel furnaces emit about 70-75% fly ash and 20-25% bottom ash whereas slag tap furnaces result in 20-25% fly ash and 70-75% bottom ash. Limestone injected for SO_2 removal would increase fly ash burden of slag tap furnaces to a greater degree than on pulverized fuel furnaces because of the above ratio. For example: On a unit consuming 100 tph of coal with 3% S and 15% ash and if 1 stoichiometric unit of limestone injected were to remove 15% of the SO_2 present, the fly ash burden on a slag tap unit would increase by 144%. Under the same condition a pulverized fuel furnace would experience a 56% increase in fly ash. Probably little or none of the injected limestone would fall into the bottom slag to alter its viscosity.

Tubular air heaters are often used with slag tap furnaces. The presence of greater fly ash quantities would probably cause adverse operational problems of gas inlet end erosion and accelerate deposits.

Gas recirculation ducts and fans would also be subjected to more severe operating conditions because of higher dust loading.

REFERENCES

(In Main Text)

1. National Academy of Engineering, "Abatement of Sulfur Oxide Emissions from Stationary Combustion Sources" COPAC-2, Ad Hoc Panel of Sulfur Dioxide from Stationary Combustion Sources, National Research Council, Washington, D.C., 1970.
2. Tennessee Valley Authority, "Sulfur Oxide Removal From Power Plant Stack Gas: Sorption by Limestone or Lime Dry Process" Conceptual Design and Cost Study. 1968. Report No. PB 178-972 clearing house for Scientific and Technical Information, Springfield, Virginia.
3. Zentgraf, Karl-Martin, "A Contribution to the Determination of Sulfur Dioxide in Flue Gases and Desulfurization of Flue Gas with Earth Alkali Metal Compounds." ***Fortschritteberichte VDI Zeitschrift***, 3 No. 22, October 1967.
4. Ishihara, Yoshime, "Kinetics of the Reaction of Calcined Limestone with Sulfur Dioxide in Combustion Gases" presented at Dry Limestone Injection Process Symposium, Gilbertsville, Kentucky, June 22-26, 1970.
5. Schwartz, S. H. and R. N. Salzman, Final Report on "Experimental Investigation of the Penetration and Dispersion Phenomena in the Limestone Injection Method," June 30, 1969-April 29, 1971. NAPCA Contract CPA-22-69-149.
6. Tanaka, K., "Desulphurization by Lime" paper presented at Third Limestone Symposium, Clearwater, Florida, December 4-8, 1967.
7. Kruel and Juntgen, H., "On the Reaction of Calcined Dolomite and Other Alkaline Earth Compounds with SO_2 of Combustion Gases as Carried Out in a Cloud of Suspended Dust," Translated by U.S.P.H.S.
8. Goldschmidt, K., "Experiments for Removal of Sulphur Dioxide from Flue Gases," paper presented at Third Limestone Symposium, Clearwater, Florida, December 4-8, 1967.
9. Bituminous Coal Reasearch, Inc., "Research On Methods For Control of Sulfur Dioxide Emissions From Coal-Burning Power Boilers," BCR Report L-273 to Electric Research Council and National Coal Association. BCR, Inc., 350 Hochberg Road, Monroeville, Pennsylvania, March 7, 1968, 88 pp.
10. Hatfield, J. D., Y. K. Kim, R. C. Mullins, and G. H. McClellan, "Investigation of the Reactivities of Limestone to Remove Sulfur Dioxide from Flue Gas," 1971, TVA Division of Chemical Development, Fundamental Research Branch, Muscle Shoals, Alabama 35660.
11. Borgwardt, R. H. "Kinetics of the Reaction of SO_2 with Calcined Limestone" paper presented at the Symposium on Limestone Sulfur Dioxide Reaction Kinetics and Mechanisms, Cincinnati, Ohio, February 5-6, 1969.
12. Potter, A. E., "Sulfur Oxide Capacity of Limestones" American Ceramic Society Bulletin Vol. 48, pp. 855-858, No. 9, September 17, 1969.

13. Coutant, R. W., et al, "Investigation of the Reactivity of Limestone and Dolomite for Capturing SO_2 from Flue Gas." Battelle Memorial Institute, Columbus Laboratories, 505 King Avenue, Columbus, Ohio, November 20, 1970.

14. Dever, Garland R., Jr., and Preston McGrain, "High Calcium and Low Magnesium Limestone Resources in the Region of the Lower Cumberland, Tennessee, and Ohio Valleys, Western Kentucky," Kentucky Geological Surveys, Series X, Bulletin 5, 1969.

15. Attig, R. C. and P. Sedor, "Additive Injection for Sulfur Dioxide Control, A Pilot Plant Study," Babcock & Wilcox Research Center Report 5460. Sponsored by NAPCA.

16. Borgwardt, R. H., et al, "Selected Studies on Alkaline Additives, Sulfur Dioxide Control" E.P. A. Office of Air Programs Publication No. APTD-0737, p. 133, December 1971.

17. Harvey, R. D., "Petrographic and Mineralogical Characteristics of Carbonate Rocks Related to Sulfur Dioxide Sorption in Flue Gases" Final Report to Air Pollution Control Office of EPA, Contract No. CPA 22-69-65, July 15, 1971.

18. Attig, R. C. and A. F. Duzy, "Coal Ash Deposition Studies and Application to Boiler Design *Proceedings of the American Power Conference 1969*, Vol. 31, pp. 290-300.

19. Wagoner, C. L., "Reheater Deposits in Unit No. 10, Shawnee Station, TVA, Babcock & Wilcox unpublished report dated May 21, 1971.

20. Thomas, D. G., Oak Ridge National Laboratories, Oak Ridge, Tennessee. Private Communication.

21. Thomas, D. G., "Dry Limestone Injection: Factors Affecting the Reaction of SO_2 with Limestone Particles," Dry Limestone Injection Process Symposium, Gilbertsville, Kentucky, June 22-26, 1970. (Final paper dated August 1970)

22. Clay, David T., "Residence Time Calculations" Unpublished In-house research, Office of Air Programs, Control Systems Division, September 2, 1971.

23. Chrusciel, R. T., "Research Into the Effect of Introducing Dolomite Into Boiler on the Disposition of Coals to Form Deposits on Heating Surfaces." Power Metrology Research Organization "Energopomiar" Poland. EPA foreign research agreement 05-302-3.

24. Reid, W. T., "Basic Factors in the Capture of Sulfur Dioxide by Limestone and Dolomite," Paper No. 69-PWR-5 presented at the Joint ASME-IEEE Power Generation Conference, Charlotte, N.C., Sept. 21-25, 1969.

BIBLIOGRAPHY

A. References on Background of Dry Processes

(Used by permission of Bituminous Coal Research, Inc., "Research on Methods for Control of Sulfur Dioxide Emissions from Coal-Burning Power Boilers," B.C.R. Report L-273, March 7, 1968, pp. 46-52.)

1. "Adsorption," Chapter from "Chemical Engineers' Handbook," 3rd ed., by J. H. Perry, New York, N.Y.: McGraw-Hill, 1950. p. 916, "Properties of Magnesia."

   Gives sulfur adsorption data for active MgO.

2. Arai, Yasuo, Takenouchi, Hiroshi, and Nagai, Shoichiro, "Calcination of $CaCO_3$ and SO_2 absorption by CaO," Sekko To Sekkai 44, 5-11 (1960); Chem. Abstr. 54, 12536g (1960).

   This is a dry process which studied absorption of SO_2 with quicklime. Reaction was carried out between SO_2 from coal combustion gas and CaO, which was prepared in an electric furnace heated from 18-1400°C. When velocity of SO_2 was held at 200 cc/min, no reaction occurred at $<400°$C and the metastable region of $CaSO_4$ and CaS in at 400°-800°C. The $CaSO_3$ and CaS changed to $CaSO_4$ at $>800°$C and the $CaSO_4$ decomposed at $>1000°$. Charted data show that SO_2 absorption by quicklime increases up to 1000°C.

3. Azbe, V. J., "Rationalizing smoke abatement," Third Int. Conf. Bituminous Coal, Carnegie Tech., Pittsburgh, Pa., 1931.

   This bound booklet describes air pollution conditions, refers to firing practices for all fuels and includes much data obtained on St. Louis conditions. Author advocates briquetting all coals of sulfur above one percent with lime before burning.

4. Beuschlein, W. L., "The recovery of SO_2," Chem. Abstr. 31, 2424 (1937).

   SO_2 absorbed in limestone towers for sulfite production.

5. Bienstock, D., Field, J. H., and Myers, J. G., "Process development in removing sulfur dioxide from hot flue gases," U.S. Bur. Mines, Rept. Invest. 5735 (1961).

   This is a dry process using a simulated flue gas of CO_2, SO_2 and humidified air and nitrogen. This gas was then used with many metal oxides and alkalized alumina. Results show SO_2 absorbed/100 gms of absorbent. Regenerating systems also included for alumina, MnO and activated carbons.

6. Bienstock, D., Field, J. H., and Myers, J. G., "Removal of sulfur oxides from flue gases with alkalized alumina at elevated temperatures (625°F)," Fuel Abstr. 6, 114 (1965).

   The Bureau of Mines reports continuous method for removing SO_2 from waste gases. Contaminants are absorbed directly by alkalized alumina. Covered by two patents: U.S. 2,992,884 and 3,150,923.

7. Billinge, B. M. H., "The chemisorption of sulfur dioxide on carbons," Central Electricity Research Laboratories, Cleeve Road, Leatherhead, Surrey, England, Laboratory Note No. RD/L/N 154/64.

8. Bowles, O., "Metallurgical limestone; problems and products," U.S. Bur. Mines, Bull. 299, p. 40 (1929).

This bulletin contains all knowledge up to this time on quarrying, mining, preparation, and utilization of metallurgical stone. Value as a flux is discussed, including impurities.

9. Bratton and Brindley, "Kinetics of vapour phase hydration of MgO. Part 2. Dependence of temp. plus H_2O vapour pressure," Trans. Faraday Soc. 61 (509). Part 5 (May 1965).

10. Bretsznajder, S., "Systems of SO_2 and CO_2 with CaO," Chem. Abstr. 27, 5624 (1933).

This article describes the dry process of CaO absorbing CO_2 and SO_2 even when the pressure of the gas is much lower than the equilibrium pressure of the system.

11. Bretsznajder, S., "Utilization of SO_2 in industrial flue gases," Chem. Abstr. 47 (1953).

This is a review of various methods of absorbing SO_2 from waste gases and a discussion of advantages and disadvantages of both.

12. Briner, E. and Monnier, R., "$CaCO_3$ reaction with dry SO_2," Chem. Abstr. 24, 1813 (1930).

This article contains reactions of sulfurous anhydride on the carbonate and phosphate of calcium. At ordinary temp., dry SO_2 as liquid or gas has no appreciable action even after months on $CaCO_3$ but at 95° exothermic reaction occurs. Below this temp., no reaction occurs. From 350-450°, the $CaSO_4$ formed was as high as 47 percent.

13. "Clay catalysts," Chem. Abstr. 53, 7573g (1959).

This reference concerns MgO in clay catalysts and treatment with O_2-SO_2 mixtures.

14. Colby, S. F., "Occurrence and uses of dolomites in the United States," U.S. Bur. Mines, Inform. Circ. 7192, p. 21 (1941).

This is a dry process using limestones and dolomites for sulfur gas absorption. High magnesian dolomites undesirable because they disintegrate and clog tower.

15. "Crushing and grinding," Chapter from "Chemical Engineers' Handbook," 3rd ed., by J. H. Perry, New York, N.Y.: McGraw-Hill, 1950. p. 1154.

Describes grinding of quicklime in a ball mill.

16. Cunningham, W. A., "Fundamentals of lime burning," Ind. Eng. Chem. 43, 635-38 (1951).

Lime is calcined between 600°-1200°C. Dissociation can result from excessive heating. Lime then may not hydrate and has low CaO content.

17. Curran, G. P., Clancey, J. T., Scarpiello, D. A., Fink, C. E., and Gorin, E., "Carbon dioxide acceptor process," Chem. Eng. Progr. 62 (2), 80-6 (1966).

This article describes manufacture of pipeline gas from lignite char and using dolomite as CO_2 acceptor. Dolomite regenerator feature is included and considerable tabulated data.

18. "Effect of dolomite additions to boiler furnaces on the sulfur dioxide content of the stack gases. Unit No. 18, Fisk Station."

This is a report from the U.S.P.H.S., describing dolomite additions to No. 18 unit furnace of the Fisk Station. Identification missing. Results showed quantities needed to reduce SO_2 content.

19. Emley, W. E., "Manufacture of lime," U.S. Bur. Stds., Circ. 337 (1927).

This circular contains account of the methods used in making quicklime and hydrated lime. Descriptions of nine plants are included. All phases of manufacture are treated in detail and methods for determining available CaO or $Ca(OH)_2$ are explained.

20. Furnas, C. C., "The rate of calcination of limestone," Ind. Eng. Chem. 23 (5), 534-8 (1931).

This method describes the phase relationships between $CaCO_3$ and CaO. Curves and data show calcination rates. Explanation covers the progress of calcination from surface to inner areas of particles.

21. Garner, W. E., "The kinetics of endothermic solid reactions," Chapter from "Chemistry of the Solid State," New York, N.Y.: Academic Press, 1955. p. 217.

The chapter on kinetics contains a discussion of dehydration rates of dolomite, $CaCO_3$ and the term nucleation is used as a specific property of solids.

22. "Giant fume catcher stops fluoride emission," Chem. En. 65 (24), 66 (1958).

This is the story of United States Steel's fluorine removal system at their Provo, Utah, plant.

Calcium compds. tie up fluorine. Powdered limestone is mixed with sinter charge. Cottrell collectors used with 20 percent humidity environment because CaF_2 dry would not take electrical charge.

23. Glenn, R. A. and Zawadzki, E. A., "Catalytic gas-phase oxidation and removal of sulfur oxides from flue gases," Fuel Abstr. 5 (1), 557 (1964).

Used vanadium and alumina catalysts at 750°-800° C.

24. Graf, D. L. and Goldsmith, J. R., "Some hydrothermal synthesis of dolomite and protodolomite," J. Geol. 64, 173-86 (1956).

The object of this work was to determine the conditions needed to prepare dolomite from carbonates. Temp. of about 500°C needed. In nature, long exposure under aqueous conditions will do the same thing.

25. Haagen-Smit, Arie J., "Industrial sources of air pollution; (2) Electric power plants (gas and oil fuels)," Proc. of Nat. Conf. on Air Pollution, Washington, D.C., 146-55, 1958.

This is a joint project by Southern Calif. Edison Co. of Los Angeles and describes injection of limestone, lime, and alk. additives into furnace and gas stream. SO_3 removal data included and test conditions.

26. Hayes, H. S., "Dry process for removal of SO_2" Fuel Abstr. 3 (10), 107 (1962).

This process describes the need for a dry method and suggests electrostatic and centrifugal force. Electrically charged Turbo-blower is equipment involved here. Sulfur not mentioned.

27. Hein, L. B. (TVA Wilson Dam), "Removal of sulfur dioxide from power plant gases," TVA Monthly Report 47-A, 63-74 (Mar. 1955).

    This work discarded use of wet slurries. Their pilot plant was used to test limestones and dolomites. Contact times were important and plans at that time were to get more data on this phase.

28. Ilinski, M., "An examination of the reaction between CaO and SO_2 by means of the flow method," Roczniki Chem. 12, 799 (1932).

    This article describes absorption of SO_2 by CaO. Amount and temperatures given. Specific mixtures of SO_2 and N_2 were used.

29. Illinski, M., "Reaction of lime with SO_2," Chem. Abstr. 29 6129 (1935).

    This article shows percentage decomposition vs pressure curves.

30. Kelley, K. K., "Contributions to the data on theoretical metallurgy," U.S. Bur. Mines, Bull. 584 (1960).

    This includes extensive data on heat contents and entropy of CaO, MgO.

31. Kirov, N. Y., "Sulfur in oil fuels - Its effects in combustion," J. Inst. Fuel 35, 426-31 (1962).

    Formation of SO_3 has been studied by conversion from SO_2. Atomic oxygen listed as most important for conversion in flames. Catalytic converters studied were ferric and vanadium oxides, ferric sulfate and effect of hot metal surfaces.

32. Kiyoura, Raisaku, "SO_2 stack gas gives $(NH_4)_2$ SO_4," Chem. Eng. News 44 (26), 23 (June 1966).

    This new dry process removes SO_2 from stack gas and converts it into $(NH_4)_2$ SO_4 by direct gas-phase reaction. Oxidation of SO_2 done by V_2O_5. Ammonia injected into system.

33. Knibbs, N. V. S., "Design and operation of modern lime works," Cement and Lime Manufacture 10, 4-11, 49-62 (1937).

    This chapter describes all phases of lime making, including plant equipment, operating details and quality control.

34. Kruel, M. and Juntgen, H., "On the reaction of calcined dolomite and other alkaline earth compounds with SO_2 of combustion gases as carried out in a cloud of suspended dust."

    This is a translation furnished by U.S.P.H.S. which describes desulfurization work on a pilot plant scale. Tubular reactor used and limes and dolomite dusts were injected. SO_2 reduction measured by difference in content in and out. Amounts required showed 4.5 times stoichiometric requirements to get 100 percent desulfurization.

35. Kurtzrock, R. C., Bienstock, D., Field, J. H., "Process development in removing SO_2 from hot flue gases. Laboratory scale pulverized coal-fired furnace," Fuel Abstr. 5 (1002), 90 (1964).

    A laboratory scale pulverized coal-fired furance was built in this process to supply 250 to 1000 ft^3/hr flue gas. It can be run intermittently or continuously.

36. Lessing, R., "The sources of atmospheric pollution," Annual Conference of National Smoke Pollution Society, Bristol, England, 1935. pp. 2-20.

Describes sulfur conditions in England - tabulating $CaCO_3$ required for SO_2 water needed to neutralize SO_2 and dissolve $CaSO_4$.

37. Markant, H. P., McIlroy, R. A., and Matty, R. E., "Absorption studies—MgO - SO_2 systems," Tappi 45 (11), 849-54 (1962).

Pilot system results on absorption characteristics of MgO - SO_2 extensive tabulated data on other factors involved.

38. Mitsubishi Heavy Industries, "Test of a pilot plant of dry type SO_2 elimination process," Aminoil, Inc., Central P.O. Box 1453, Tokyo, Japan.

Uses dry process for SO_2 removal plus mechanical and electrical collectors.

39. Nakagawa, S., "Recovery and utilization of sulfur dioxide in waste gases by the JECCO process," Fuel Abstr. 6, 132 (1965).

40. Pechkovskii, V. V., "Reaction of SO_2 with metal oxides," Chem. Abstr. 51, 1437c, 16067h (1958).

Describes reaction rates SO_2 with metal oxides in presence of carbon.

41. Pechkovskii, V. V., et al, "Reaction of SO_2 with $CaCO_3$ in oxidizing atmospheres," Khim. i Khim. Teckhnol. 6 (6), 991-6 (1963); Chem. Abstr. 61, 276h (1964).

This work describes high pressure reactions of $CaCO_3$ with SO_2-air mixtures. These reactions were studied by differential thermal analysis and X-ray crystallography. SO_2 in oxidizing atmosphere reacts energetically with CaO made by decomposing limestone above 700°C. Sulfitization may begin at 300°-500°C. $CaSO_3$ reacts with air in presence of SO_2 to give $CaSO_4$ as temp. goes from 500° to 800°.

42. Pinear, V. A., "Lime for removing sulfur dioxide from gases," Fuel Abstr. 4, 3866 (1963).

Gases are cleaned, then lime is used without cooling the gases.

43. Piper, J. D. and Van Vliet, H., "Effect of temperature variation on composition, fouling tendency and corrosiveness of combustion gas from a pulv. fired steam generator," Trans. ASME 80, 1251-63 (1958).

Metal condensers placed in stack gas stream. Deposits noted and SO_2 partial pressures recorded.

44. "Process Furnaces," Chapter from "Chemical Engineers' Handbook," 3rd ed., by J. H. Perry, New York, N. Y.: McGraw-Hill, 1950. p. 1610.

Dolomite kilns data. This gives operating parameters and production details.

45. "Removal of SO_2," Fuel Abstr. 4 (3), 1999 (1963).

Eliminates dust using filters.

46. "Reversibility of reactions between SO_2 and lime and between CaS and $CaSO_4$," Roczniki Chem. 10, 715-27 (1930); Chem. Abstr. 25, 1174 (1931).

This article gives detailed information on the reactions involved including equilibrium and dissociation conditions.

47. Russell, J. L., Sc. D. Thesis, Mass. Inst. Technol., Cambridge, Mass., 1955.

This work describes apparatus used for pressure drop-flow rate relationships for CO_2 at reaction temperatures.

48. Schlenk, R. and Hammerschmidt, F., "Equilibrium study of the system calcium-sulfur oxides," Z. Für Anorg. Chem. 210, 305-12 (1933).

This chapter is a physical chemistry study of the reactions involving $CaSO_4$ + S, CaO + SO_2, CaS + SO_2. Data are plotted and temperature, pressure relationships are tabulated.

49. Seil, G. E., "Gas Chemists Manual of Dry Box Purification of Gas," New York, N.Y.: American Gas Association, 1943.

This textbook contains a section on gas purifying materials. CaO is one of these and a test method is given. Section also includes a total sulfur method in fouled unmixed oxides, CO_2 determination in limestone, H_2S in gases, and use of lime for gas purification.

50. Squires, A. M., "An introduction to the top heat cycle," Proc. Am. Power Conf. 28 (1966).

This paper outlines method of using oxygen flame to raise steam to 1500° F. Included is a system for cleaning gases using CaO and MgO to eventually produce elemental sulfur. Diagrams are also included with all phases of the processes involved.

51. Squires, A. M., "Economics of the top heat cycle using residual oil," Symp. on Economics of Air Pollution Control, A.I.Ch.E., Columbus, Ohio, 1966.

This A.I.Ch.E. paper describes top heat cycle which means adding extra heat to high-pressure steam in form of combustion products. Fixed bed of calcined dolomite used.

52. Stone, Robert L., "Thermal analysis of magnesite at CO_2 pressures up to 6 atm," Metal Ceramic Interactions IV (Jan. 1954).

53. "Sulfur-smoke removal system," Mech. Eng. 86 (8), 58 (1964); Iron and Steel Eng. 41, 167 (1964).

This is a report of Pennsylvania Electric Company installation at Seward, Pa., where solids and SO_2 are removed from stack gases.

54. Tadokaro, Y., Science Report of Tohoku Imp. Univ. of Japan 10, 339 (1921-22).

This work reports the thermal conductivity of calcium oxide as .4 Btu/hr/ft/°F.

55. Tamayo, P., "High temperature reaction rates of carbon dioxide and calcium oxide," B. S. Thesis at Mass. Inst. Technol., 1956.

This is a theoretical lab. study on absorption of CO_2 by CaO and $CaCO_3$. Reaction rates vs time and temperature are shown and extensive data are included.

56. Tarbutton, G., et al, "Recovery of SO_2 from flue gases," Ind. Arts Index, 2002 (1957).

Ozone and manganese process.

57. Taylor, H. S., "Industrial Hydrogen," New York, N. Y.: The Chemical Catalog Co., Inc., 1921.

This textbook describes hydrogen making and purifying. Refractory oxides are used for purifying including lime to absorb CO_2. Details of the absorbing reaction are given.

58. "Test of a pilot plant of dry type SO_2 elimination process," Aminoil, Inc., Central P.O. Box 1453, Tokyo, Japan.

This is a laboratory scale dry process later done in a power station. Powdered MgO used. NH_3 and oxygen introduced, by-products described.

59. Uno, T., "Desulfurizing reaction of lime," Tetsu-To-Hagane, No. 1, 22 (1951), published by Iron & Steel Institute of Japan, 195 abstracts.

This is a very short paragraph on CaO + FeS reaction and related complexes. Energy for this reaction is also included.

60. Whittingham, G., "High temp. reactions of coal minerals during combustion," Brit. Coal Util. Res. Assoc. Monthly Bull. 18, 581-91 (1954).

Information shows sulfur combines primarily with Ca and Mg.

61. Wickert, K., "Experiments on desulfurization before and after the burner for reducing the release of SO_2," Mitt. VGB, No. 83, 74-82 (Apr., 1963).

CaO and MgO as desulfurizers and relation of temp. to absorption.

62. Wickert, K., "Removal of sulfur, vanadium, and alkalies from heating and combustion gases," Chem. Abstr. 58, 8826g (1963).

CaO and MgO were used to purifygases. Fe_2O_3 and V_2O_5 can be used as oxidizing catalysts. Alkaline compounds are removed by adding SiO_2 or Al_2O_3.

63. Wilson, H. and Skinner, K. G., "Occurrence, properties, and preparation of limestone and chalk for whiting," U.S. Bur. Mines, Bull. 395 (1937). p. 160.

This bulletin gives results of a study undertaken to encourage the use of domestic materials in making whiting. Chalk, limestone, and marble are described.

64. Zalogin, N. G., "Protecting the atmosphere from pollution by flue gas from large power stations," Fuel Abstr. 3 (1) (1962).

This is an evaluation of a sulfur extraction process not described except that tall chimneys are used to disperse the gases. This comparison study concerned ash and sulfur contents in power station fuels of the USSR.

65. Zawadzki, "Knowledge of the systems calcium-sulfur-oxygen," Z. Für Anorg. Chem. 205, 180-92 (1932).

This article gives detailed data on temperatures and pressures of SO_2 adsorption by lime. The information includes the physical chemistry and energy equations.

66. Zawadzki, J. and Syryczynski, Z., "Reversibility of reactions between SO_2 and lime and between CaS and $CaSO_4$" Roczniki Chem. 10, 715-27 (1930); Chem. Abstr. 25 (1931).

B. General References

1. Goksøyr, H. and K. Ross, "Determination of Sulfur Trioxide in Flue Gas," ***J. Inst. of Fuel***, 1962, 35, pp. 177-179.
2. Borgwardt, R. H. and R. D. Harvey, "Properties of Carbonate Rocks Related to SO_2 Reactivity," ***Environmental Science & Technology***, April 1972, pp. 350-360.
3. Reid, W. T., "Basic Factors in the Capture of Sulfur Dioxide by Limestone and Dolomite," Paper No. 69-PWR-5 presented at the Joint ASME-IEEE Power Generation Conference, Charlotte, N. C., Sept. 21-25, 1969.
4. McClellan, G. H., "Physical Characterization of Calcined and Sulfated Limestones" 4th Dry Limestone Symposium, Gilbertsville, Ky., June 22-26, 1970.
5. M. W. Kellogg Co., "Availability of Limestone and Dolomites," Task 1, EPA Contract CPA 70-68.
6. M. W. Kellogg Co., "Review of the Dry Limestone Process," Task 3, Final Report for Phase I. EPA Contract CPA 70-68, May 1, 1972.
7. Corey, R. C., "Measurement of Gas Temperatures with Thermocouples," ***Combustion***, October 1956, pp. 47-55.
8. Whitten, C. M., and R. G. Hagstrom, "Pilot Plant Moving Grate Furnace Study of Limestone-Dolomite for Control of Sulfur in Oxide Combustion Flue Gas," Final Report on Contract PH-22-68-68, Chemcoke Division, Peabody Coal Co., May 27, 1969.
9. Boynton, R. S., ***Chemistry and Technology of Lime and Limestone***, Interscience New York, N.Y., 1966.
10. Sage, W. L., and J. B. McIlroy, "Relationship of Coal Ash Viscosity to Chemical Composition," ***ASME Transactions***, 1960, Vol. 82, pp. 145-155.
11. Tougher, E. H., "Identification of Test Methods for Determinating the Degree of Burning of Limestones," ***Final Report*** Battelle Memorial Institute, Columbus, Ohio, November 13, 1968.
12. Diehl, E. K., "Limestone Addition As A Means of Reducing Sulfur Dioxide Emission From Power Plants," B.C.R., Inc., Report L-364, May 14, 1970.
13. Womble, T. D., Jr., and J. T. Reese, Part I - Equipment Description, Calibration and Operating Experience. Part II - Preliminary Test Results.
    Elder, H. W., Part III - Test Program.
    Morris, J. S., Part IV - Solid Waste and Water Quality Considerations "The Dry Limestone Injection Process For SO_2 Control, Unit Full-Scale Evaluation," 4th Dry Limestone Symposium, Gilbertsville, Kentucky, June 22-26, 1970.
14. Falkenberry, H. L. and A. V. Slack "Removal of SO_2 From Power Plant Stack Gases by Limestone Injection" American Institute of Chemical Engineers 61st Annual Meeting, Los Angeles, California, December 1-5, 1968.